Supporting Information

Calibration and Evaluation of PUF-PAS Sampling Rates across the Global Atmospheric Passive Sampling (GAPS) Network

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Contents

PUF-PAS Effective Volume Model Version 2 (Matlab File)

The Matlab script, developed and run in Matlab version R2016a, for calculating PUF-PAS Effective Volume is attached as a Matlab file (**PUF_PAS_Effective_Volume_Modelv2.m**).

Processing ISD Weather Data (Matlab File)

The Matlab script, developed and run in Matlab version R2016a, for processing the appropriate ISD weather data, to be used in the PUF-PAS Effective Volume model, is attached as a Matlab file (**process_isd_metdatav2.m**).

Chemical Descriptors (CSV File)

For compounds of interest, the model requires the physical-chemical properties, such as molecular weight (MW), octanol-air partitioning coefficient (K_{oa}) at 25 °C, and internal energies of octanol–air transfer (dU_{oa}). Alternatively, the user could decide to use the linear free energy relationship (LFER) to predict K_{PUF} for compounds of interest partitioning to polyurethane foam (PUF) disks. The physical-chemical properties and LFER descriptors[1, 2] for all 209 PCB congeners are given in an accompanying CSV (**Chemical_Descriptors.csv**) file that is critical to use in the PUF-PAS Effective Volume Model. Ensure this file is in the same workspace as the PUF-PAS Effective Volume Model script.

Steps to Run Effective Volume Model (PDF File)

A step-by-step README file to assist with identifying an appropriate weather station, downloading the correct weather data, processing the data with the provided script, and setting up a run to obtain congener and deployment specific effective sampling volumes is provided as a PDF.

Calibration Process

The fitting term gamma (γ) was determined from a calibration dataset of sampling rates determined using depuration compounds as described in the manuscript. We evaluated the relationship of the analytically determined gamma with site predictors (sampling site, elevation, latitude, and longitude), deployment predictors (quarter of the year, year, and length of deployment), chemical predictors (K_{oa} and molecular weight) and weather predictors (temperature, wind speed, pressure, and water-vapor mixing ratio). We used multiple linear regression and non-linear regression trees to determine if gamma was a function of any of these predictors. For a smaller calibration sample set deployed in Chicago, we reported that gamma was a function of air temperature, wind speed, and K_{oa}.[3] We did not find this to be the true for the GAPS calibration sample set. In fact, our previous method for calculating gamma showed a high bias between modelled and depuration-determined sampling rates from samples deployed in Chicago ([3, 4]). The mean bias was 24%, 96%, 44%, -14%, and 43% for ^{13}C PCB-9, ^{13}C PCB-15, ^{13}C PCB-32, PCB-30, and d_6-γ-HCH, respectively, consistent with erroneous results of the model in environments outside the original calibration range [specifically at high wind speeds (Figure S1)]. The poor prediction of Rs for very high and very low wind speeds demonstrated the need to perform a recalibration with a more diverse dataset, while also providing a comparative baseline performance level for the recalibration. (Note: In the new version of the flowrate model it is NOT possible to get one of these erroneous values. This pitfall has been fixed by the recalibration process.)

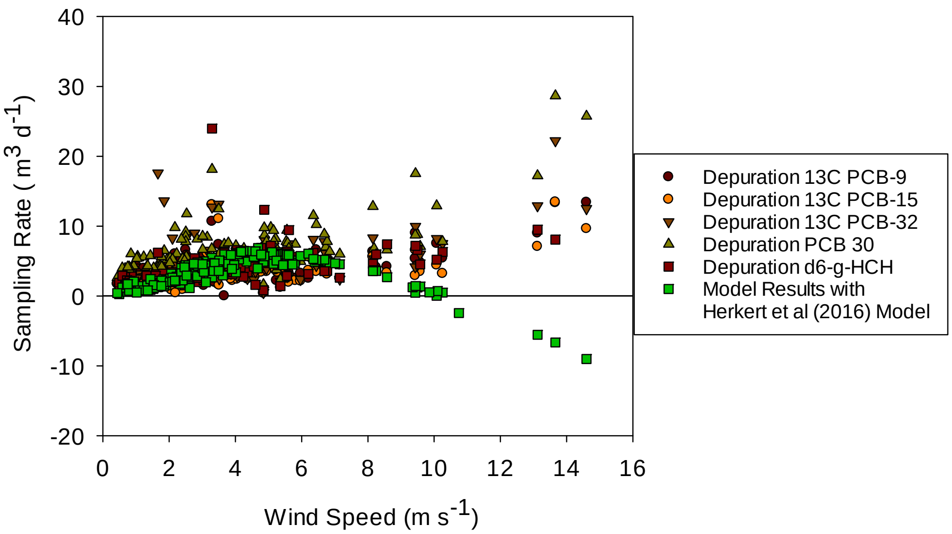

Figure S1: Predicted R_s values calculated using Herkert et al. (2016) and reported R_s using depuration compounds. The Herkert et al (2016) model was calibrated using samples deployed in Chicago. It is apparent that at wind speeds below 2 m s^{-1} and at wind speeds above 6 m s^{-1} the R_s predicted by Herkert et al, (2016) (green squares) diverge from R= calculated from the depuration compounds.

Table S1: Summary of bias for the original Chicago calibration[3] presented in Petrich et al (2013) and Herkert et al (2016). The bias is the difference between the modelled R_s and using depuration compounds.

	BIAS	*ERROR*
^{13}C PCB-9	24%	41%
^{13}C PCB-15	96%	99%
^{13}C PCB-32	44%	63%
PCB-30	-14%	26%
d6-g-HCH	43%	61%

The site predictors were removed from the final calibration because the regression tree isolated specific sites rather than generalizable relationships (Figure S2). The chemical predictors, including K_{oa}, did not provide a statistically significant correlation with the calculated gamma-values (Figure S3). There was also no significant correlation between the calculated gamma-values and any of the deployment or weather predictors (Figure S4).

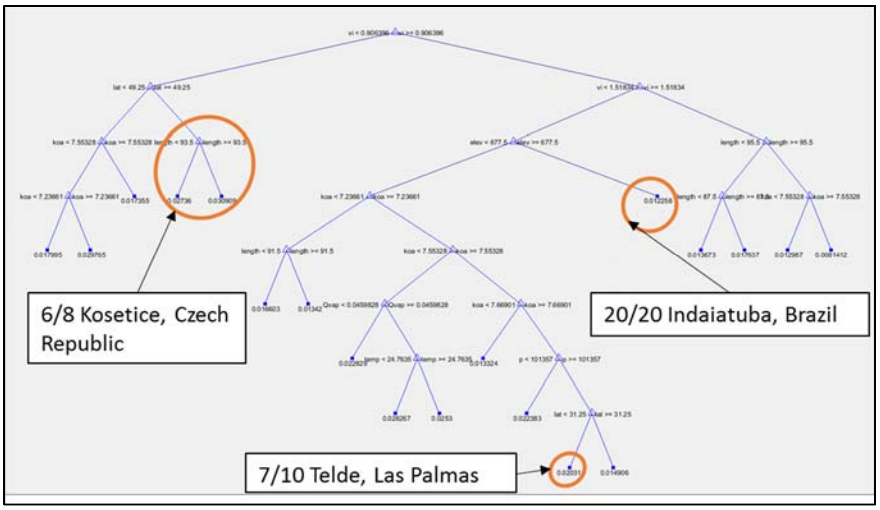

Figure S2: Example of the regression tree approach isolating individual sites in the results from depuration compounds for 2006. The results of this analysis showed that gamma was independent of geographical location.

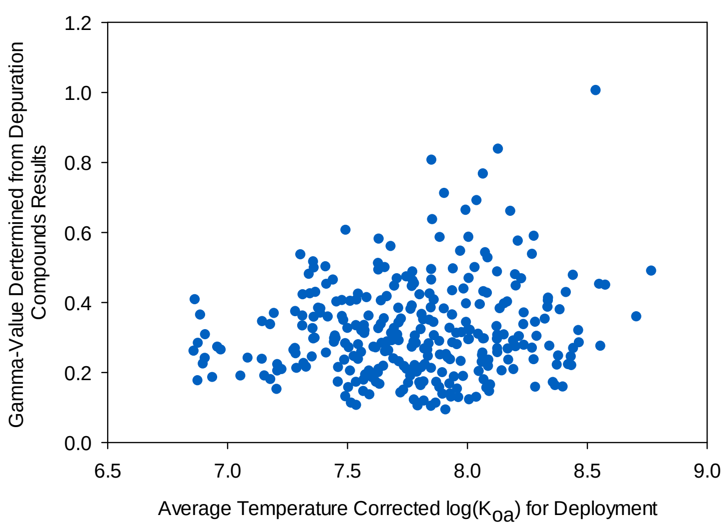

Figure S3: Scatter plot of all gamma-values determined from depuration compound results used in the recalibration versus the average temperature corrected log(Koa) for the depuration compound. This figure demonstrates the inability to statistically differentiate between the available depuration compounds by log(Koa). The results of this analysis showed that gamma was independent of Koa.

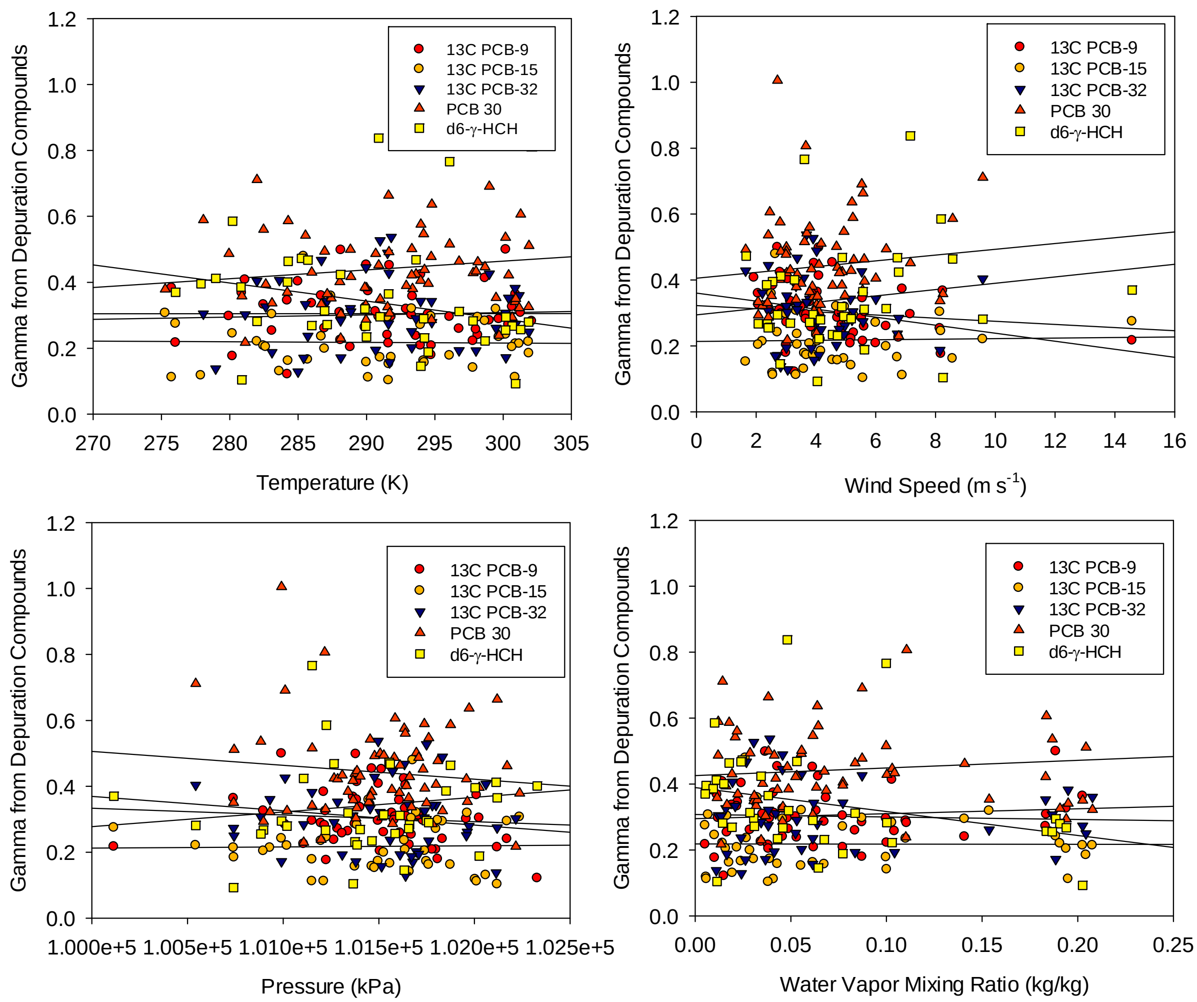

Figure S4: Scatter plot of all gamma-values determined from depuration compound results used in the recalibration versus average weather parameters for each of the deployments. This figure demonstrates the inability to statistically differentiate between the available depuration compounds by weather parameters. The results of this analysis showed that gamma was independent of weather parameters.

The unlabeled PCB-30 depuration compound was excluded from the final calibration because it was repeatedly flagged as an outlier when compared to the other depuration compounds when constructing regression trees under any conditions. The best result was a constant gamma for all deployments and compounds determined with a regression tree using a leave-one-out cross-validation method. The constant gamma-value was determined to be 0.267 when implementing the ISD weather dataset and 0.315 when implementing MERRA. The two datasets fundamentally offer something different so it is expected they produced different calibration factors. The MERRA dataset offers complete global coverage of observationally constrained modelled gridded weather values, while the ISD dataset offers sparse global coverage of observed local values that tends to report less precise measurements than MERRA (i.e. integer wind speeds). The difference in calibrated gamma between the two datasets is small, indicating that both datasets provide similar calibration against the depuration compound method. Table S2 compares the bias and error (|bias|) in modeled R_S using the two weather data sources and the previous calibration method with Chicago data.[3, 4]

Table S2: Summary of bias of the R_S values for the two sources of weather data: the Integrated Surface Database (ISD) and the Modern Era Retrospective-Analysis for Research and Applications (MERRA). The bias is the difference between the modelled R_s and using depuration compounds.

	BIAS		*ERROR*	
	ISD	MERRA	ISD	MERRA
^{13}C PCB-9	4%	6%	24%	33%
^{13}C PCB-15	37%	31%	46%	47%
^{13}C PCB-32	4%	-1%	29%	36%
PCB-30	-35%	-34%	35%	37%
d6-g-HCH	1%	0%	35%	38%

The prediction for sampling rates determined from depuration compounds ^{13}C PCB-9, ^{13}C PCB-32, and d_6-γ-HCH performs well for both weather data sources and produce average bias near 0%. Although ^{13}C PCB-15 still displays a bias of around 30%, it is substantially reduced from the bias of over 90% using the Chicago sample set for calibration Herkert et al (2016). The only compound that increased in bias from the original to new calibration was the unlabeled PCB-30. This is unsurprising given that PCB-30 was removed from the final calibration dataset.

Table S3: Summary of the calibration sample set.

GAPS Calibration Dataset	
# of Samples	82
# of Sites	24
# of Continents	6
Years deployed	2006-2007
Depuration Compounds (DC)	^{13}C PCB 9, ^{13}C PCB 15, ^{13}C PCB 32, PCB 30, Lindane
Depuration Quality Criteria	DC loss > 60% Obvious Outliers Removed (i.e. negative, etc.) Normalized to stable DC (^{13}C PCB 107)
ISD Weather Quality Criteria	Minimum of 3 hour time interval No "gaps" of any parameter > 72 hours Station in close proximity to sampler deployment location

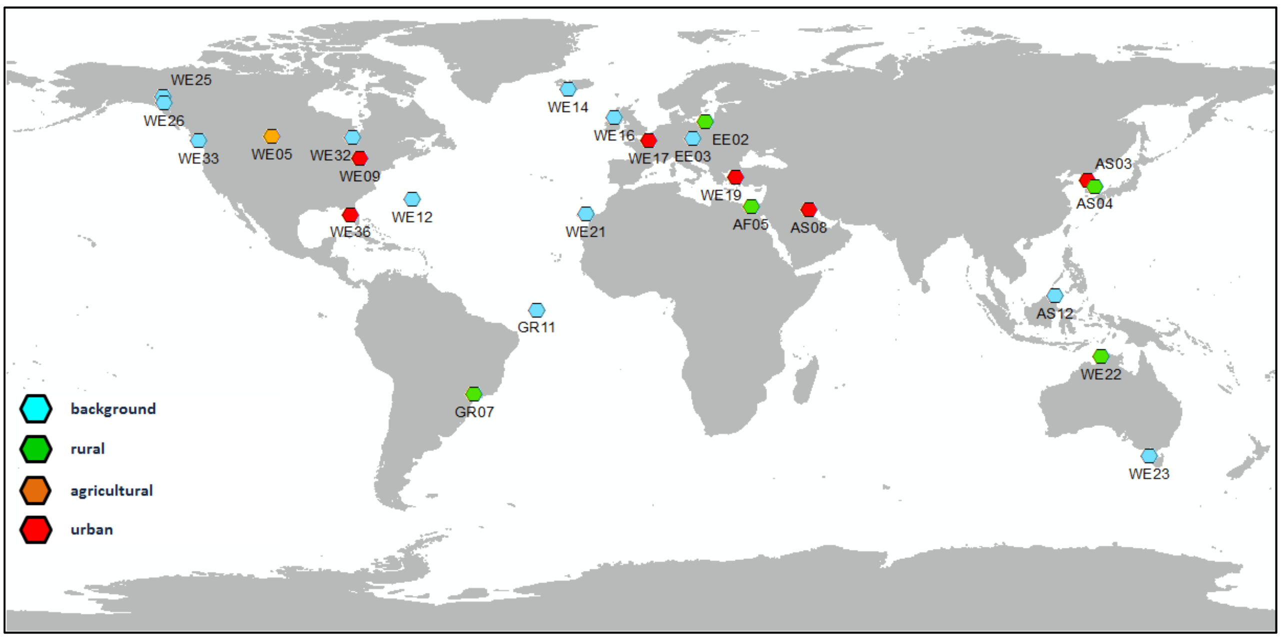

Figure S5: Map of the 24 sites used in this study for calibration of the gamma value.

Table S4: Description of PUF-PAS air samples used in this study to calibrate gamma. The R_s values calculated from depuration compounds noted as N/A were eliminated based on the quality criteria summarized in Table S3.

Site ID	Country	Longitude	Latitude	Start Date	End Date	ISD Station ID	Depuration Results ($m^3 d^{-1}$)				
							^{13}C PCB9	^{13}C PCB15	^{13}C PCB32	PCB30	d6g-γ-HCH
AF05	Egypt	31.6	30.1	2/1/2006	4/25/2006	623660-99999	3.7	3.4	4.6	5.1	N/A
AS08	Kuwait	47.9	29.3	1/24/2006	3/27/2006	405820-99999	4.8	2.2	N/A	5.8	3.1
AS12	Malaysia	117.8	5.0	1/18/2006	4/18/2006	964910-99999	2.8	2	3	4.1	2.9
GR07	Brazil	-47.2	-23.2	2/2/2006	5/4/2006	837210-99999	3.4	2	2.3	4.5	1.2
WE12	Bermuda	-64.7	32.4	1/31/2006	5/11/2006	780160-13601	4.4	2.5	2.4	6	2.6
WE16	Ireland	-7.3	55.4	1/26/2006	5/8/2006	039800-99999	4.5	N/A	5.3	6.8	N/A
AF05	Egypt	31.6	30.1	4/25/2006	7/12/2006	623660-99999	N/A	4.8	5.8	7.2	3.9
EE02	Poland	18.5	54.2	3/31/2006	6/30/2006	121460-99999	3.6	N/A	N/A	4.5	N/A
EE03	Czech Republic	15.1	49.6	4/3/2006	6/30/2006	116280-99999	3.5	N/A	N/A	4.5	N/A
GR07	Brazil	-47.2	-23.2	5/4/2006	8/6/2006	837210-99999	3.1	1.9	1.7	4	2.4
WE09	Canada	-79.5	43.8	4/13/2006	7/14/2006	712650-99999	4.2	N/A	N/A	5.1	3.9
WE12	Bermuda	-64.7	32.4	5/11/2006	8/9/2006	780160-13601	N/A	3.4	5	6.6	4.4
WE16	Ireland	-7.3	55.4	5/8/2006	7/6/2006	039800-99999	4.8	N/A	6.1	7	N/A
WE17	France	2.4	48.9	3/16/2006	6/15/2006	071560-99999	2.7	N/A	3.5	3.7	N/A
WE19	Turkey	27.1	38.4	4/4/2006	7/4/2006	172190-99999	6	4.3	3.9	8.7	5.9
WE21	Spain	-15.4	28.0	4/4/2006	7/5/2006	600250-99999	N/A	3.5	3.9	7.8	4.7

WE23	Australia	144.7	-40.7	4/5/2006	6/14/2006	949540-99999	4.2	3.3	N/A	6.6	7.4
AS08	Kuwait	47.9	29.3	8/27/2006	11/28/2006	405820-99999	N/A	4.3	4.6	7.4	6.2
EE02	Poland	18.5	54.2	6/30/2006	9/30/2006	121460-99999	3.3	N/A	N/A	4.1	6.2
EE03	Czech Republic	15.1	49.6	6/30/2006	10/2/2006	116280-99999	3.8	N/A	N/A	5	2.6
GR07	Brazil	-47.2	-23.2	8/6/2006	11/11/2006	837210-99999	N/A	2.6	2.4	5.4	3.4
WE05	Canada	-104.7	50.2	6/30/2006	10/5/2006	718630-99999	4.6	N/A	2.3	5.7	4.2
WE09	Canada	-79.5	43.8	7/14/2006	10/13/2006	712650-99999	3.9	N/A	N/A	5.4	3.4
WE16	Ireland	-7.3	55.4	7/6/2006	10/8/2006	039800-99999	5.6	3.1	4.8	7.8	3.6
WE17	France	2.4	48.9	6/15/2006	9/19/2006	071560-99999	3.9	2	2.2	4.6	2
WE19	Turkey	27.1	38.4	7/4/2006	10/9/2006	172190-99999	4.8	3.6	4.4	7.8	5.9
WE21	Spain	-15.4	28.0	7/5/2006	10/4/2006	600250-99999	N/A	4.8	5.7	9.8	7.2
WE22	Australia	130.9	-12.4	8/1/2006	10/3/2006	941200-99999	4	2.8	4.2	5.8	3.7
AS08	Kuwait	47.9	29.3	11/28/2006	1/17/2007	405820-99999	4.2	N/A	N/A	6	N/A
EE02	Poland	18.5	54.2	9/30/2006	12/31/2006	121460-99999	4.2	N/A	N/A	5.2	N/A
EE03	Czech Republic	15.1	49.6	10/2/2006	1/2/2007	116280-99999	3.2	N/A	N/A	4	N/A
WE16	Ireland	-7.3	55.4	10/8/2006	1/23/2007	039800-99999	4.8	3.5	6	7.1	4.5
WE17	France	2.4	48.9	9/19/2006	12/21/2006	071560-99999	1.7	N/A	N/A	2.6	N/A
WE19	Turkey	27.1	38.4	10/9/2006	1/11/2007	172190-99999	3.5	N/A	N/A	5.1	N/A
WE21	Spain	-15.4	28.0	10/4/2006	1/3/2007	600250-99999	N/A	3.7	5.5	8.2	4.8

WE22	Australia	130.9	-12.4	10/3/2006	1/8/2007	941200-99999	N/A	3.3	4.1	6.2	4.1
AS03	Korea	127.0	37.6	1/29/2007	3/30/2007	471080-99999	2.99	N/A	N/A	4.78	N/A
AS04	Korea	129.3	36.0	1/29/2007	4/3/2007	471380-99999	2.13	N/A	N/A	N/A	N/A
EE02	Poland	18.5	54.2	1/17/2007	3/31/2007	121460-99999	3.25	N/A	N/A	4.52	N/A
GR11	Brazil	-29.3	0.9	2/1/2007	4/6/2007	824000-99999	3.90	3.73	4.73	6.77	2.64
WE12	Bermuda	-64.7	32.4	1/30/2007	3/28/2007	780160-13601	4.66	N/A	N/A	6.35	N/A
WE14	Iceland	-20.3	63.4	1/18/2007	3/31/2007	040480-99999	13.41	9.63	12.52	25.73	N/A
WE16	Ireland	-7.3	55.4	1/23/2007	4/17/2007	039800-99999	4.09	N/A	N/A	5.89	5.96
WE21	Spain	-15.4	28.0	1/3/2007	4/9/2007	600250-99999	4.37	4.07	5.28	7.59	4.66
WE22	Australia	130.9	-12.4	1/16/2007	4/2/2007	941200-99999	2.68	2.38	2.82	4.71	6.58
AS12	Malaysia	117.8	5.0	3/27/2007	6/26/2007	964910-99999	4.30	1.38	1.94	4.27	N/A
EE02	Poland	18.5	54.2	3/31/2007	6/30/2007	121460-99999	3.93	N/A	N/A	5.45	N/A
EE03	Czech Republic	15.1	49.6	4/5/2007	6/29/2007	116280-99999	3.88	N/A	2.81	5.62	N/A
GR07	Brazil	-47.2	-23.2	3/31/2007	7/3/2007	837210-99999	2.19	N/A	N/A	3.30	N/A
GR11	Brazil	-29.3	0.9	4/6/2007	6/30/2007	824000-99999	2.93	3.21	3.39	4.78	2.27
WE05	Canada	-104.7	50.2	4/2/2007	6/27/2007	718630-99999	3.52	N/A	2.75	4.93	6.37
WE09	Canada	-79.5	43.8	4/11/2007	7/3/2007	712650-99999	3.97	2.87	4.05	5.87	N/A
WE12	Bermuda	-64.7	32.4	3/28/2007	7/3/2007	780160-13601	3.24	2.13	2.37	4.93	N/A
WE21	Spain	-15.4	28.0	4/17/2007	7/17/2007	600250-99999	3.98	5.09	6.50	7.87	N/A

WE25	Canada	-135.6	61.3	5/17/2007	9/12/2007	719640-99999	5.41	6.12	6.54	8.41	3.15
WE26	USA	-135.4	59.5	5/15/2007	9/11/2007	703620-25335	2.01	N/A	N/A	3.02	N/A
WE32	Canada	-81.6	49.9	3/30/2007	6/29/2007	718310-99999	5.31	3.06	3.54	7.60	N/A
WE33	Canada	-125.5	48.9	3/7/2007	7/3/2007	711060-94234	3.94	2.12	2.74	5.57	N/A
AS12	Malaysia	117.8	5.0	6/26/2007	10/2/2007	964910-99999	3.71	1.15	1.88	4.17	1.58
EE02	Poland	18.5	54.2	6/30/2007	9/30/2007	121460-99999	5.27	3.11	4.29	8.13	2.49
EE03	Czech Republic	15.1	49.6	6/29/2007	10/1/2007	116280-99999	5.69	3.13	4.59	8.55	4.63
GR07	Brazil	-47.2	-23.2	7/3/2007	10/7/2007	837210-99999	3.25	1.64	2.53	4.94	N/A
WE05	Canada	-104.7	50.2	6/27/2007	10/3/2007	718630-99999	4.79	5.16	8.09	9.76	12.34
WE09	Canada	-79.5	43.8	7/3/2007	10/3/2007	712650-99999	2.86	1.54	2.45	4.48	N/A
WE12	Bermuda	-64.7	32.4	7/3/2007	10/3/2007	780160-13601	3.09	2.97	3.46	5.69	1.59
WE16	Ireland	-7.3	55.4	7/3/2007	10/2/2007	039800-99999	5.93	5.59	8.11	11.52	6.16
WE17	France	2.4	48.9	6/29/2007	10/1/2007	071560-99999	2.72	N/A	2.44	4.23	N/A
WE21	Spain	-15.4	28.0	7/17/2007	10/17/2007	600250-99999	3.34	5.19	7.48	6.83	9.45
WE22	Australia	130.9	-12.4	6/29/2007	10/1/2007	941200-99999	N/A	2.43	3.22	4.87	5.69
WE32	Canada	-81.6	49.9	6/29/2007	9/28/2007	718310-99999	3.41	N/A	N/A	4.85	N/A
WE33	Canada	-125.5	48.9	7/3/2007	10/2/2007	711060-94234	3.45	N/A	2.54	5.36	N/A
WE36	USA	-82.2	28.0	7/3/2007	10/3/2007	722110-12842	2.89	2.60	3.29	5.07	1.51
AS12	Malaysia	117.8	5.0	10/2/2007	12/25/2007	964910-99999	3.38	1.16	1.80	3.99	N/A

EE03	Czech Republic	15.1	49.6	10/1/2007	1/2/2008	116280-99999	3.75	N/A	N/A	5.43	N/A
WE09	Canada	-79.5	43.8	10/3/2007	1/10/2008	712650-99999	2.21	N/A	N/A	3.74	N/A
WE12	Bermuda	-64.7	32.4	10/3/2007	1/8/2008	780160-13601	3.32	1.95	2.86	5.62	N/A
WE16	Ireland	-7.3	55.4	10/2/2007	1/1/2008	039800-99999	6.34	5.60	8.31	12.82	4.61
WE17	France	2.4	48.9	10/1/2007	1/9/2008	071560-99999	1.50	N/A	N/A	2.77	N/A
WE21	Spain	-15.4	28.0	10/17/2007	1/17/2008	600250-99999	3.57	3.40	4.99	6.84	6.89
WE22	Australia	130.9	-12.4	10/1/2007	1/9/2008	941200-99999	N/A	2.67	3.50	5.32	N/A
WE33	Canada	-125.5	48.9	10/2/2007	12/24/2007	711060-94234	2.74	N/A	N/A	4.30	N/A
WE36	USA	-82.2	28.0	10/3/2007	1/3/2008	722110-12842	4.14	2.49	3.49	6.64	3.07

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