

Simulation Model of Reactive Nitrogen Species in an Urban Atmosphere using a Deep Neural Network: RNDv1.0

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Abstract

Nitrous acid (HONO), one of the reactive nitrogen oxides (NO_y), plays an important role in the formation of ozone (O_3) and fine aerosols ($\text{PM}_{2.5}$) in the urban atmosphere. In this study, a new simulation approach to calculate HONO mixing ratios using a deep neural technique based on measured variables was developed. The 'Reactive Nitrogen species simulation using Deep neural network (RND)' has been implemented in Python. The first version of RND (RNDv1.0) was trained, validated, and tested with HONO measurement data obtained in Seoul during the several months from 2016 to 2021.

RNDv1.0 was constructed utilizing k-fold cross validation and evaluated with an Index Of Agreement (IOA), correlation coefficient (r), Root Mean Squared Error (RMSE), and Mean Absolute Error (MAE). The RNDv1.0 adequately represents the main characteristics of the measured HONO and thus, RND v1.0 is proposed as a supplementary model for calculating the HONO mixing ratio in a polluted urban environment.

31 1. Introduction

32

33 Surface ozone (O_3) pollution has been reported to be worsen over continental areas
34 (Arnell et al., 2019;Monks et al., 2015;Varotsos et al., 2013;IPCC, 2014). In particular, a
35 warmer climate is expected to increase surface O_3 concentrations and peak levels in polluted
36 regions, depending on its precursor levels (IPCC 2021). As one of the short-lived climate
37 pollutants (SLCPs), O_3 also interacts with the global temperature via positive feedback
38 (Shindell et al., 2013;Myhre et al., 2017;Stevenson et al., 2013). Therefore, it is imperative to
39 accurately predict the mixing ratios and variations of surface O_3 . While operational models such
40 as community multiscale air quality (CMAQ) have been used widely for this purpose,
41 uncertainties still arise from poorly understood chemical mechanisms involving reactive
42 nitrogen oxides (NO_y) and volatile organic compounds (VOCs), and lack of their measurements
43 (Mallet and Sportisse, 2006;Canty et al., 2015;Akimoto et al., 2019;Shareef et al., 2019;Cheng
44 et al., 2022).

45 In the urban atmosphere, NO_y typically includes NO_x ($NO + NO_2$), HONO, HNO_3 ,
46 organic nitrates (e.g., PAN), NO_3 , N_2O_3 , and particulate NO_3^- . These species are produced and
47 recycled through photochemical reactions until they are removed through wet or dry deposition
48 (Liebmann et al., 2018;Brown et al., 2017;Wang et al., 2020;Li et al., 2020). NO_y play an
49 important role in critical environmental issues concerning the Earth's atmosphere, spanning
50 from local air pollution to global climate change (Sun et al., 2011;Ge et al., 2019). The oxidation
51 of NO to NO_2 , and finally to HNO_3 , is the backbone of the chemical mechanism producing
52 ozone (O_3) and $PM_{2.5}$ (particulate matter of size $\leq 2.5 \mu m$), and it determines the oxidization
53 capacity of the atmosphere. Recently, as O_3 has increased along with a decrease in NO_x emission
54 over many regions including East Asia, interest in the heterogeneous reaction of reactive
55 nitrogen oxides, which is yet to be understood, has been newly raised (Brown et al.,
56 2017;Stadtler et al., 2018). Currently, the lack of measurement of individual NO_y species
57 hindered a comprehensive understanding of the heterogeneous reactions (Anderson et al.,
58 2014;Wang et al., 2017b;Chen et al., 2018b;Akimoto and Tanimoto, 2021;Stadtler et al., 2018).

59 In particular, there are growing number of evidence for heterogeneous formation of
60 HONO in relation to high $PM_{2.5}$ and O_3 occurrence in urban areas (e.g., (Li et al., 2021b). As

61 an OH reservoir, HONO will expedite the photochemical reactions involving VOCs and NO_x
62 in the early morning, leading to O₃ and fine aerosol formation. Nonetheless, its formation
63 mechanism has not been elucidated clearly enough to be constrained in conventional
64 photochemical models. In addition to the reaction of NO with OH (Bloss et al., 2021), various
65 pathways of HONO formation have been suggested from laboratory experiments, field
66 measurements, and model simulations: direct emissions from vehicles (e.g., (Li et al., 2021a)
67 and soil (e.g.,(Bao et al., 2022), photolysis of particulate nitrate (e.g., (Gen et al., 2022),
68 heterogeneous conversion of NO₂ on various aerosol surfaces (e.g., (Jia et al., 2020), ground
69 surface (e.g.,(Meng et al., 2022), and microlayers of sea surface (e.g., (Gu et al., 2022). Among
70 these, the heterogeneous reaction mechanism on the surface is of major interest in the recent
71 HONO study.

72 HONO has been measured mostly during intensive campaigns in urban areas using
73 various techniques such as a LOng Path Absorption Photometer (LOPAP) (Kleffmann et al.,
74 2006;Xue et al., 2019), Chemical Ionization Mass Spectrometry (CIMS) (Levy et al.,
75 2014;Roberts et al., 2010), Ion Chromatography (IC) (VandenBoer et al., 2014;Gil et al.,
76 2020;Ye et al., 2016;Xu et al., 2019), Monitor for AeRosols and Gases in ambient Ari (MARGA)
77 (Xu et al., 2019), and Quantum Cascade - Tunable Infrared Laser Differential Absorption
78 Spectrometry (QC-TILDAS)(Lee et al., 2011;Gil et al., 2021). Of these methods, QC-TILDAS
79 has served as a reference for intercomparison of measurement data from different techniques
80 due to high time resolution and stability (Pinto et al., 2014). These studies reported the
81 maximum HONO of several ppb levels at nighttime. In comparison, the model captured at most
82 67~90 % of the observed HONO in megacities such as Beijing (Tie et al., 2013;Liu et al., 2019).

83 In recent years, Machine Learning (ML) method has been adopted in the atmospheric
84 science for pattern classification (e.g. New Particle Formation event) and forecasting and
85 spatiotemporal modelling of O₃ and PM_{2.5} (Arcomano et al., 2021;Shahriar et al.,
86 2020;Krishnamurthy et al., 2021;Cui and Wang, 2021;Joutsensaari et al., 2018;Chen et al.,
87 2018a;Kang et al., 2021). Among ML methods, the Neural Network (NN) architecture is widely
88 used owing to its powerful ability to process large amounts of data, allowing improvement in
89 the performance of conventional models through being integrated with physical equations
90 (Reichstein et al., 2019;Schultz et al., 2021). As a NN architecture, a multi-layer artificial neural
91 network, referred to as a Deep Neural Network (DNN), employs a statistical method that learn

92 non-linear relations in data and obtain the optimum solution for the target species without prior
93 information on the physicochemical processes. DNN has advantages over other NN architecture
94 such as Convolution NN (CNN) or Long-Short Term Memory (LSTM) because it works well
95 for discrete spatiotemporal data. In general, the performance of DNN is similar to or better than
96 other ML methods for small number of data as well as large data set (Baek and Jung, 2021; Dang
97 et al., 2021; Sumathi and Pugalendhi, 2021).

98 When the DNN method is applied to atmospheric chemical constituents, it requires
99 large amount of data for training and thus, the size of measurement data becomes a limiting
100 factor for trace species such as HONO, which are not routinely measured such as O₃ or PM_{2.5}.
101 In this regard, the daily average HONO mixing ratio was attempted to be estimated using
102 ensemble ML models with satellite measurements (Cui and Wang, 2021). In comparison, the
103 hourly HONO mixing ratio was calculated using a simple NN architecture with measured
104 variables, which were thought to be deeply involved in the formation of HONO (Gil et al.,
105 2021). The accuracy of the hourly HONO estimated from input variables such as aerosol surface
106 areas and mixed layer height was better than the daily HONO estimate.

107 The aim of this study is to develop a user-friendly ‘Reactive Nitrogen species
108 simulation using DNN’ model (RNDv1.0) that estimates HONO mixing ratios from real-time
109 measurements of criteria pollutants and meteorological parameters and is ultimately to be
110 incorporated into operational models that forecast urban air quality. Since this study is the first
111 attempt to calculate the HONO mixing ratio using RNDv1.0, the entire construction process is
112 described in detail, and the performance is evaluated by comparing the results with simulations
113 using a commonly used model and observations over several years.

114

115 **2. Model description**

116

117 The development of RNDv1.0 model follows the systematic steps similar to a general
118 machine learning model construction workflow, including collecting data, preprocessing data,
119 building the DNN, training and validating the model, and testing the performance of the model
120 (Figure 1). The RNDv1.0 was written in Python and necessary libraries to build and operate

121 RNDv1.0 are listed in Table 1. The dataset used to train-test-validation can be downloaded from
122 Gil et al., 2021.

123

124 **2.1. Collection of measurement data for model construction**

125

126 As the first step constructing the RNDv1.0, measurement data were obtained including
127 HONO, reactive gases, and meteorological parameters. It is noteworthy that the HONO
128 measurement data is for model construction and is not required to run the RND model. The
129 HONO mixing ratio was measured in Seoul using a QC-TILDAS system during May–June
130 2016, June 2018, and April–June 2019 (Lee et al., 2011; Gil et al., 2021) and a MARGA system
131 during May–June and October–November 2021 (Gil, 2022). When testing and evaluating
132 atmospheric HONO measurement methods, QC-TILDAS has been chosen as the reference
133 method for comparing ambient HONO mixing ratios measured using several different
134 techniques owing to its advantages of low detection limits (~ 0.1 ppbv) and high temporal
135 resolution (Pinto et al., 2014). More details on measurements can be found elsewhere (Gil et
136 al., 2021; Gil, 2022).

137 HONO was measured at Olympic Park (37.52°N , 127.12°E) during the Korea-United
138 States Air Quality (KORUS-AQ) study in 2016 (Kim et al., 2020; Gil et al., 2021), at the campus
139 of Korea University (37.59°N , 127.03°E) in 2018 and 2021, and at the site near the campus
140 (37.59°N , 127.08°E) in 2019 (NIER, 2020) (Figure S1). Although measurements were made at
141 three sites, O_3 and $\text{PM}_{2.5}$ levels have been known to be greatly influenced by the synoptic
142 circulation throughout the Korean peninsula (Peterson et al., 2019; Jordan et al., 2020), and the
143 Korea University campus and Olympic Park have served as measurement sites representing the
144 air quality of Seoul. In addition to HONO, trace gases including O_3 , NO_2 , CO , and SO_2 and
145 meteorological parameters including temperature (T), relative humidity (RH), wind speed (WS)
146 and direction (WD) were measured. Note that HONO was not significantly correlated with any
147 of these variables (Figure S2). The measurement statistics are presented in Table 2 and Table
148 S1. Briefly summarizing, the 10th and 90th percentile mixing ratios of HONO, NO_2 , and O_3 are
149 0.3 ppbv and 2.0 ppbv, 10.0 ppbv and 47.0 ppbv, and 8.0 ppbv and 75.0 ppbv, respectively for
150 the entire experiment periods.

151

152 **2.2. Data preprocessing**

153

154 In the next step, the observation data set was prepared for RNDv1.0 model construction.
155 As input variables, hourly measurements of chemical and meteorological parameters are used,
156 including the mixing ratios of O₃, NO₂, CO, and SO₂, along with temperature (T), relative
157 humidity (RH), wind speed (WS), wind direction (WD), and solar zenith angle (SZA) to
158 estimate the target species, HONO, as the output. Wind direction in degrees were converted to
159 a cosine value for continuity. As a last step in data processing, missing values were filtered out
160 from the input dataset. Finally, 54.2 % of all available measurement data (2847) were used to
161 construct and evaluate the RNDv1.0 in this study.

162 Since the measurements of these nine variables vary over a wide range in different units,
163 they were normalized to avoid bias during the calculations. Among the widely used
164 normalization methods, ‘*min-max scaling*’ method was adopted, and input variables were
165 normalized against the minimum and maximum values in this study (Eq. 1):

166

$$167 \quad x_{\text{sca}} = \frac{x_{\text{raw}} - F_2(X)}{F_1(X)}, \quad (\text{Eq. 1})$$

168

169 where x_{raw} is raw data, x_{sca} is scaled value, and F_1 and F_2 are scale factors of input
170 variable (X), which are listed in Table 2.

171

172 **2.3. Neural network architecture and hyperparameters**

173

174 At this stage, the network is built to calculate HONO using those input variables. The
175 RNDv1.0 is composed of five hidden layers (Figure 2), which employed an exponential linear
176 unit (ELU) as an activation function (Eq. 2).

177

178
$$\text{ELU} : \phi(x) = \begin{cases} e^x - 1 & (x < 0) \\ x & (x \geq 0) \end{cases}. \quad (\text{Eq. 2})$$

179

180 In a DNN, an activation function creates a nonlinear relationship between an input
 181 variable and an output variable. When constructing a DNN model, an ELU has the advantage
 182 of a fast-training process and better performance in handling negative values than other
 183 activation functions (Wang et al., 2017a;Ding et al., 2018). In addition, the mean squared error
 184 and Adam optimizer were applied as loss function and optimize function, respectively. The
 185 learning rate, epoch, and batch were set to 0.01, 100, and 32, respectively.

186

187 **2.4. Model training and k-fold cross validation**

188

189 The RNDv1.0 model was trained-and-validated and tested with HONO measurements
 190 obtained during May ~ June in 2016 and June in 2018, April ~ June 2019, and May ~ June and
 191 October ~ November in 2021, respectively (Figure 3). The number of data used for train-
 192 validation and test were 1122 and 1725, respectively.

193 With the hyperparameters specified in previous section, the performance of the model
 194 was firstly validated using the K-Fold Cross-Validation (KFCV) method, which is especially
 195 useful when the size of dataset is small (Bengio and Grandvalet, 2003). In the KFCV method
 196 (Figure 3), the entire data is randomly divided into k subsets, of which k-1 sets were used for
 197 training and the rest one was used for validation. k was set to 5 in this study. The accuracy was
 198 determined by Index Of Agreement (IOA) expressed by the following equation (Eq. 3):

199

200
$$\text{IOA} = 1 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (|P_i - \bar{O}| + |O_i - \bar{O}|)^2}, \quad (\text{Eq. 3})$$

201

202 where O_i , P_i , \bar{O} , and n are the observed value, predicted value, average of the
 203 observed values, and number of nodes, respectively.

204 As IOA vary according to the number of nodes, it was calculated for the measured
 205 (HONO_{obs}) and calculated (HONO_{mod}) mixing ratios by varying the number of nodes from 0 to
 206 100 in each hidden layer. The best performance was found with 41 nodes, with which the
 207 averaged IOA was 0.89 ± 0.01 (Figure 4). The high level of IOA demonstrates that the
 208 performance of RNDv1.0 model is adequate, and it is capable of simulating the ambient HONO
 209 mixing ratio using the routinely measured criteria pollutants and meteorological parameters.

210 The performance of RNDv1.0 was compared with that of other models, including
 211 Community Multi-scale Air Quality Model (CMAQv5.3.1, Appel et al., 2021), Random Forest
 212 (RF), and 1-layer Artificial Neural Network (ANN, Gil et al., 2021) using 2016 measurement
 213 data. A RF model was constructed using KFCV method and the same input parameters as
 214 RNDv1.0 (Figure S4). Their performance was evaluated by Mean Absolute Error (MAE), Root
 215 mean Square Deviation (RMSE), and Pearson correlation coefficient (r) (Eq. 4 - 6).

216

$$217 \quad \text{MAE} = \frac{\sum_{i=1}^n |O_i - P_i|}{n}, \quad (\text{Eq. 4})$$

$$218 \quad \text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (O_i - P_i)^2}{n}}, \quad (\text{Eq. 5})$$

$$219 \quad r = \frac{\text{cov}(O,P)}{\sigma_o \sigma_p}, \quad (\text{Eq. 6})$$

220

221 where σ and cov implies standard deviation and covariance, respectively.

222 The measured HONO mixing ratios correlated well with those calculated except for
 223 the CMAQ (Figure 5), which not only severely underestimated the measured HONO, but also
 224 failed to represent the diurnal variation (Figure 6). The statistical information about the
 225 performance of the four models is given in Table 3. The mean HONO mixing ratio measured
 226 and calculated from CMAQ, RF, ANN, and RNDv1.0 was 0.94 ppbv, 0.09 ppbv, 0.95 ppbv,
 227 0.88 ppbv, and 0.89 ppbv, respectively. Of the four models, RF showed the best performance,
 228 followed by RND. ANN has advantage of being able to calculate HONO more accurately than
 229 RND using more input variables, but it results in a lower data capture rate (41.5 %) compared
 230 to RND (97.7 %) or RF (85.3 %).

231

232 **2.6. Model test**

233

234 The RNDv1.0 and RF models were tested using June in 2018, April in 2019, and May
235 ~ June and October ~ November in 2021 (Figure 3). Of the test dataset, the early winter
236 (October ~ November) data is particularly valuable for demonstrating the applicability of the
237 RNDv1.0 because they were produced in different weather conditions from those of the train
238 dataset. Note that the RF performance was the best among the four models in train-validation
239 process (Figure 5). Interestingly, the performance of RF was much worse than RNDv1.0 in test
240 (Figure 7). The IOA and correlation coefficient of RF were extremely low (0.29 and -0.02,
241 respectively), which are similar to or worse than those for CMAQv5.3.1 (Table 3).

242 The performance of RNDv1.0 was slightly lessened, but it well tracing the HONO
243 mixing ratio. When the data in which at least one input parameters do not fall within the range
244 of the train dataset is excluded from the test dataset, there is no significant difference in the
245 performance of RNDv1.0 between the two that meet same atmospheric conditions or do not
246 meet the criteria (Figure S5 and Table S2). And this test dataset includes severe haze pollution
247 events when the daily average PM_{2.5} concentration was raised up to 120 $\mu\text{g m}^{-3}$, and the HONO
248 mixing ratio also increased to 4 ppbv or more in Seoul. Except for these extremes, RNDv1.0
249 traces well the variation of HONO mixing ratio. These test results, therefore, are convincing
250 evidence for the applicability of the RNDv1.0 to the estimation of HONO levels in the urban
251 atmosphere.

252

253 **2.6. Bootstrap test and feature importance**

254

255 A simple bootstrapping test was conducted for RNDv1.0 and RF to evaluate the relative
256 importance of the input variable to HONO concentration. In this analysis, each variable was set
257 to zero and MAE was calculated as an evaluation metrics (Kleinert et al., 2021). Of nine input
258 variables, NO₂ was found to have the most significant influence on HONO concentration,
259 followed by RH, temperature in RNDv1.0 (Table 5). The highest MAE of 0.59 ppbv can be

260 considered as the maximum uncertainty of RNDv1.0 due to the input variable. The bootstrap
261 test result is in good agreement with those of our previous study (Gil et al., 2021), where more
262 variables such as aerosol surface area and mixing layer height were incorporated into the model,
263 highlighting the crucial role of precursor gases and heterogeneous conversion in HONO
264 formation.

265 In contrast, O₃ was the most important variable for RF. This is likely due to the distinct
266 inverse relationship between O₃ and HONO in the diurnal patterns and O₃ variations over a
267 wide range. In conjunction with the evaluation of test presented in the previous section, the
268 results of feature importance for the two models demonstrates the ability of the deep learning
269 model to simulate the HONO mixing ratio more adequately in polluted urban areas compared
270 to the general machine learning model. Thus, it is reasonable to argue that the RNDv1.0
271 constructed using routinely measured criteria pollutants and meteorological parameters can
272 sufficiently capture the HONO variability in the urban atmosphere.

273

274 **3. Operation and application of RNDv1.0**

275

276 The RNDv1.0 package is provided as an operational model, .h5 files that can be opened
277 in Python. To run the RNDv1.0, the measurement data for nine input variables are required and
278 need to be properly prepared as described in Section 2.2. A sample of preprocessed input dataset
279 is provided as a .csv file (Dataset_for_model.csv). Once the input data is ready, open the
280 RNDv1.0 with input data files using the code provided in the example (Figure S3). Then, RND
281 v1.0 calculates and presents the HONO results as scaled values (x_{sca}), which will be finally
282 converted to HONO mixing ratio (ppbv) by the two scale factors in Table 2 (Eq. 5):

283

$$284 \quad \text{HONO (ppbv)} = \text{HONO}_{sca} \times F_1(\text{HONO}) + F_2(\text{HONO}). \quad (5)$$

285

286 The HONO calculated by Eq. 5 can be applied to an urban photochemical cycle
287 simulation. It is already known that the photolysis of HONO is a major source of OH radicals
288 in the early morning when the OH level is low, and this OH affects daytime O₃ formation

289 through photochemical reactions with VOCs and NO_x, which are primarily emitted during
290 morning rush hour in urban areas. In addition, the OH produced from HONO promotes the
291 photochemical oxidation of SO₂ and VOCs, leading to aerosol formation. However, the HONO
292 formation mechanism is still poorly understood, hindering O₃ and fine aerosols as well as
293 HONO from being correctly simulated in conventional photochemical models.

294 The 0-Dimension Atmospheric Modelling (F0AM) utilizing the MCM v3.3.1 chemical
295 reaction mechanisms (Wolfe et al., 2016), can be used to simulate the diurnal variation of O₃
296 with the measurements of several reactive gases (NO, NO₂, CO, HCHO, VOCs, and HONO).
297 Detailed information about F0AM can be found in
298 (<https://sites.google.com/site/wolfegm/models>) and in previous works published elsewhere
299 (Wolfe et al., 2016; Gil et al., 2020). When the F0AM model is run without HONO, it is not
300 able to reproduce the concentration and diel cycle of the observed O₃ (Figure 8). In comparison,
301 the model simulates the O₃ well within 2 ppbv when adding HONO, which is the product of
302 RND v1.0. This is mainly due to the missing OH produced by HONO photolysis in the early
303 morning. Its production rate is estimated to be 0.57 pptv s⁻¹, contributing approximately 2.28
304 pptv to OH budget during 06:00 ~ 11:00 (LST) (Gil et al., 2021). Given that OH is mainly
305 produced from the photolysis of O₃ under high sun, the early morning source of OH will
306 expedite the photochemical cycle involving NO_x and VOCs, promoting O₃ and secondary
307 aerosol formation. Since the presence of HONO in the photochemical model allows for accurate
308 estimation of OH radicals, the incorporation of RNDv1.0 into conventional models will
309 improve their overall performance.

310

311 **4. Summary and implications**

312

313 In this study, we developed the RND model to calculate the mixing ratio of NO_y in an
314 urban atmosphere using a DNN along with measurement data. The target species of RNDv1.0
315 is HONO, and its mixing ratio is calculated using criteria pollutants including O₃, NO₂, CO,
316 and SO₂, and meteorological variables including T, RH, WS, and WD, along with the SZA.
317 These variables are routinely measured through monitoring networks. The RNDv1.0 was
318 trained and validated using the HONO measurements obtained in Seoul by adopting a k-fold

319 cross validation method and tested with other HONO datasets. The test results demonstrate that
320 RNDv1.0 adequately captures the characteristic variation of HONO and confirms the efficacy
321 of RND v1.0.

322 RNDv1.0 was constructed using the measurement made in a high NO_x environment. It is
323 noteworthy that during the measurement period, the HONO mixing ratio was raised above 7
324 ppbv with the highest O₃ levels under stagnant conditions. If RNDv1.0 is applied to areas under
325 significant influence of outflows, the model possibly overestimates or underestimate the level
326 of HONO without detailed information such as nanoparticles. In the previous study, the
327 formation of HONO was shown to be intimately related with surface areas of submicron
328 particles (Gil et al., 2021). Nevertheless, the HONO concentration produced from RNDv1.0
329 with routine measurements provides the benefit of relatively inexpensive test for measurement
330 quality control, location selection, and supports the data used for traditional chemistry model
331 based on the current knowledge of the urban photochemical cycle. Therefore, it is reasonable
332 to argue that RNDv1.0 can serve as a supplementary tool for conventional forecasting models.
333 As attempts are currently being made to estimate ground HONO from satellite observations
334 (Clarisse et al., 2011;Theys et al., 2020;Armante et al., 2021), RNDv1.0 will also be useful for
335 validating satellite-derived HONO by supplementing measurement data.

336

337 **5. Acknowledgements**

338

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340 (2020R1A2C3014592) and Korea Institute of Science and Technology (KIST2E31650-22-
341 P019).

342

343 **6. Code availability**

344

345 The RND model codes (.h5 files) with preprocessed sample data can be downloaded from
346 (Gil, 2021).

347

348 **7. Author contributions**

349

350 JG and ML designed the manuscript and developed the model code. JK, GL, and JA
351 provided HONO measurements and CK provided CMAQ model data. All the authors
352 contributed to the manuscript.

353

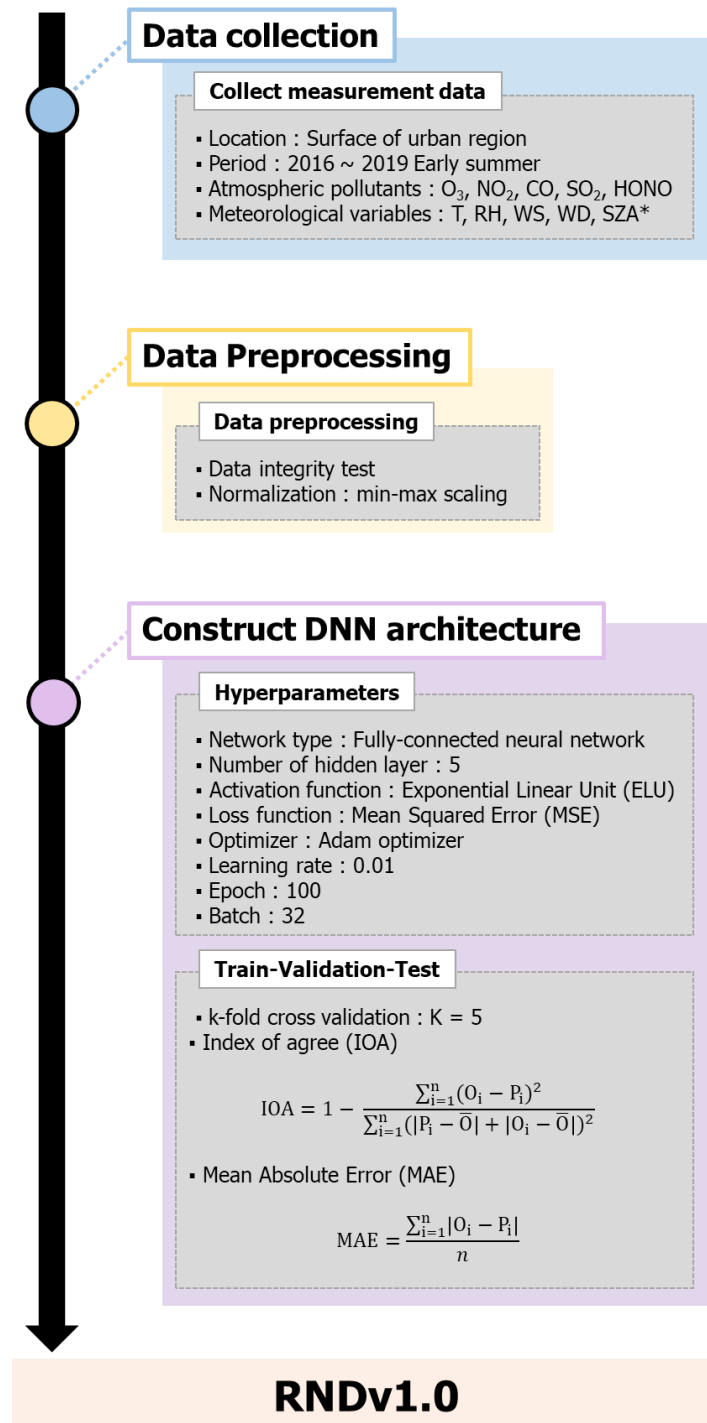
354 **8. Competing interests**

355

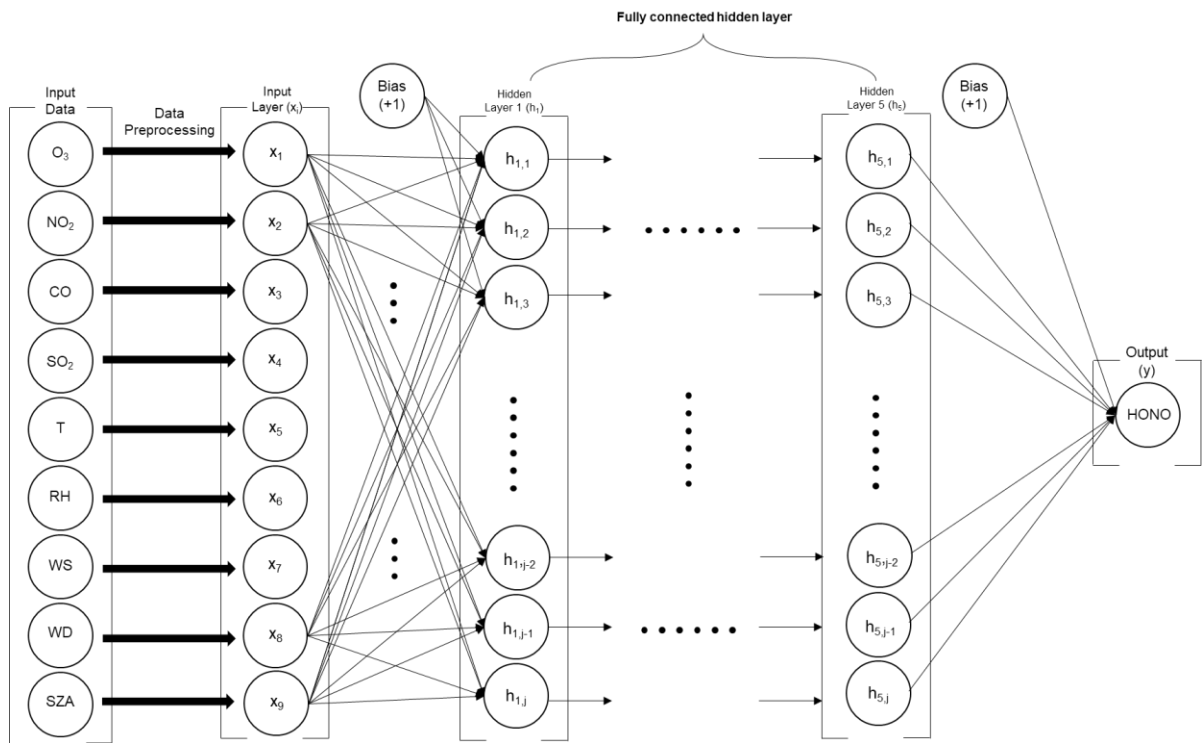
356 The authors declare that they have no conflict of interest.

357

358



362 **Figure 1.** The main processes for configuring the RNDv1.0 (*: calculated values)

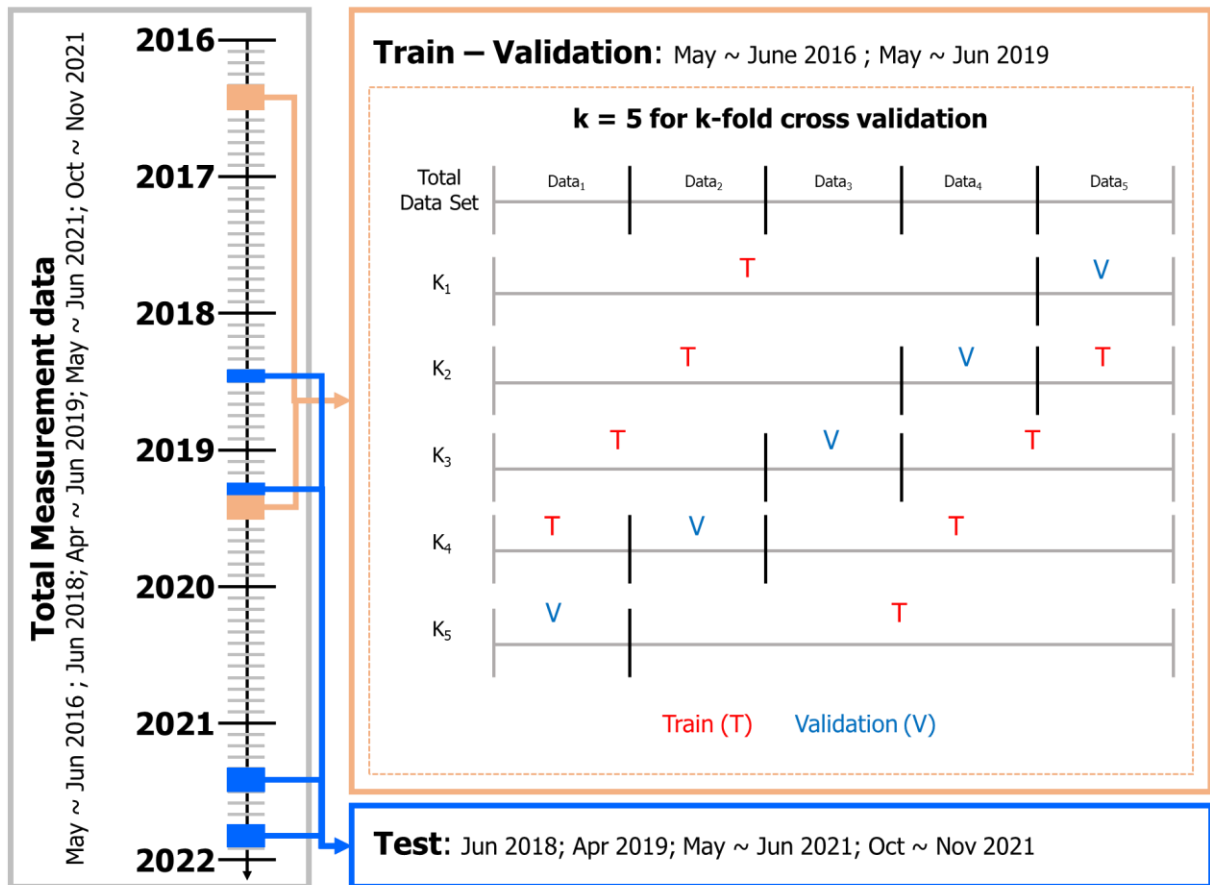


363

364 **Figure 2.** The structure of deep neural network built for RND v1.0.

365

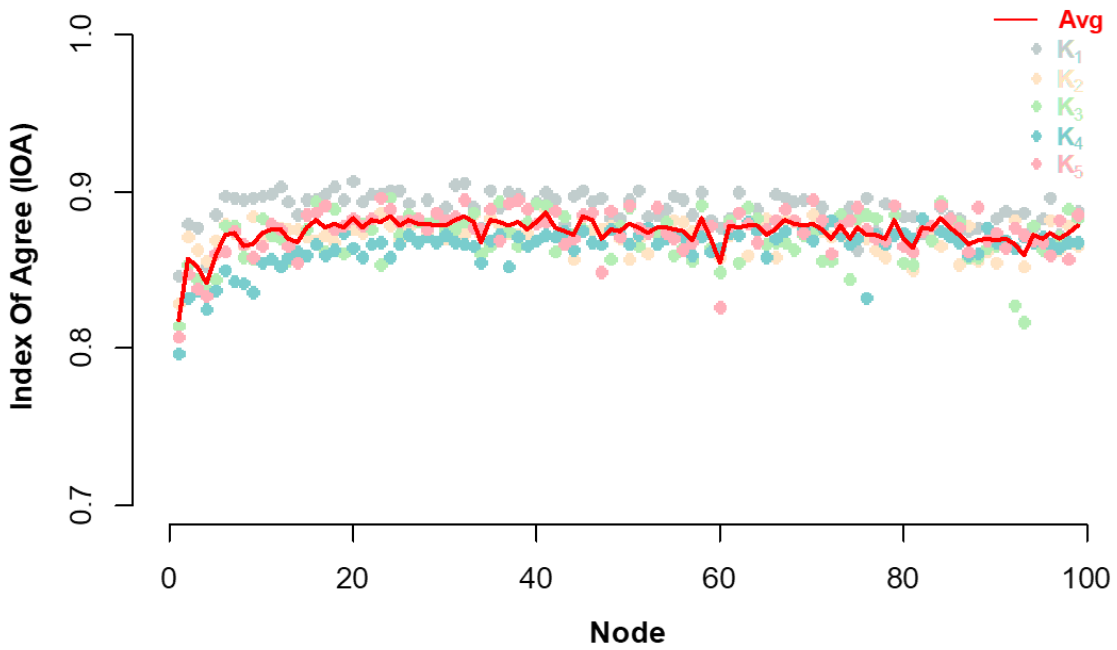
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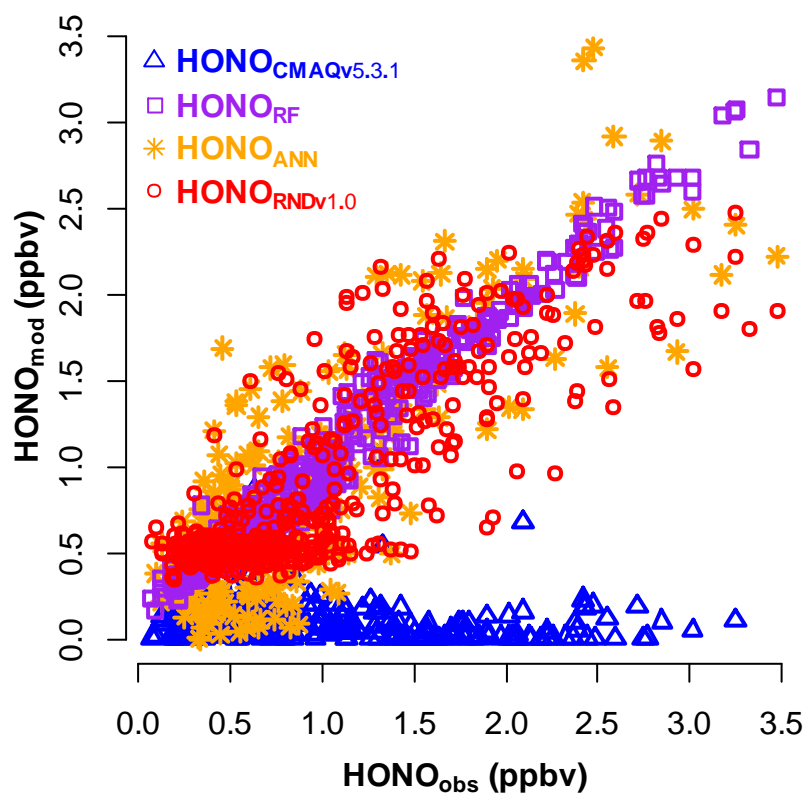
368 **Figure 3.** Design of training, validation, and test to build RNDv1.0 using measurement data.
 369 The k-fold cross validation was performed using randomly divided five subsets of training data
 370 set.

371



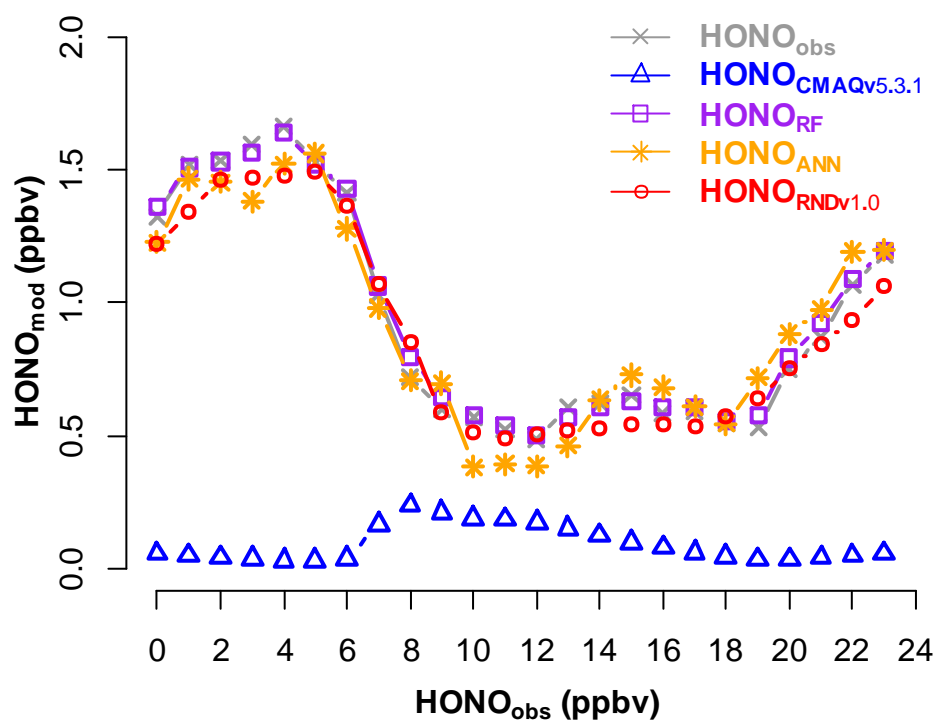
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373 **Figure 4.** Index Of Agreement (IOA) for k-fold cross validation. Solid circle and red line
 374 represent IOA for each validation (k=5) and the average of 5 validation sets at each node number



375
 376 **Figure 5.** Comparison between measured HONO (HONO_{obs}) and calculated HONO (HONO_{mod})
 377 using CMAQv5.3.1 (blue triangle), RF (purple square), ANN (orange star), and RNDv1.0 (red
 378 circle) during the KORUS-AQ campaign (may-June 2016)

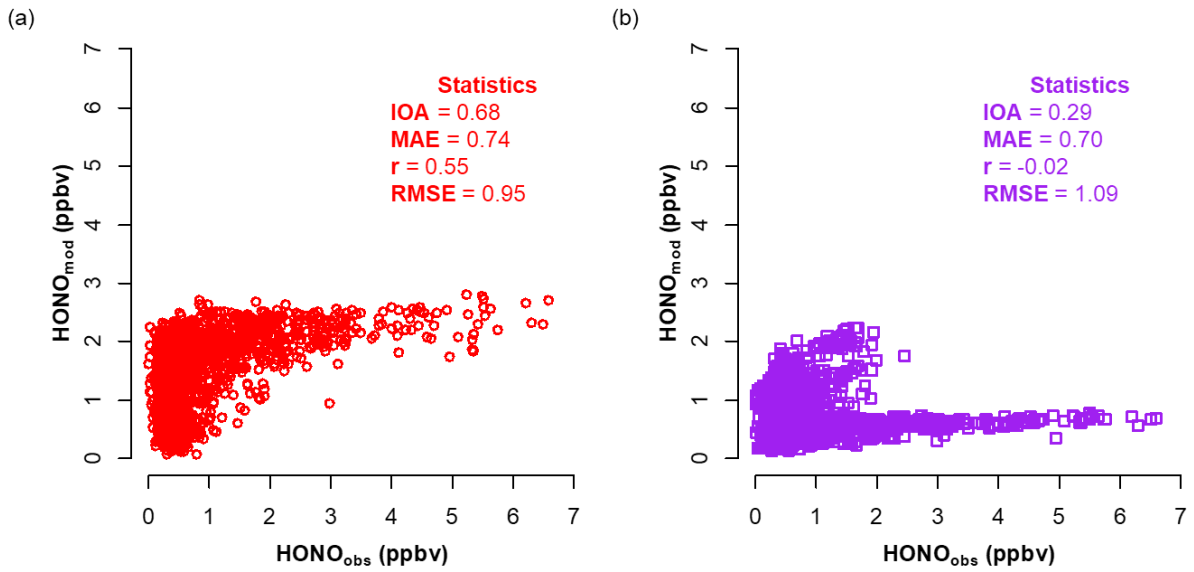
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380

381 **Figure 6.** Average diurnal variation of measured HONO (HONO_{obs}) and calculated HONO
 382 (HONO_{mod}) using CMAQv5.3.1 (blue triangle), RF (purple square), ANN (orange star), and
 383 RNDv1.0 (red circle) during the KORUS-AQ campaign (may-June 2016)

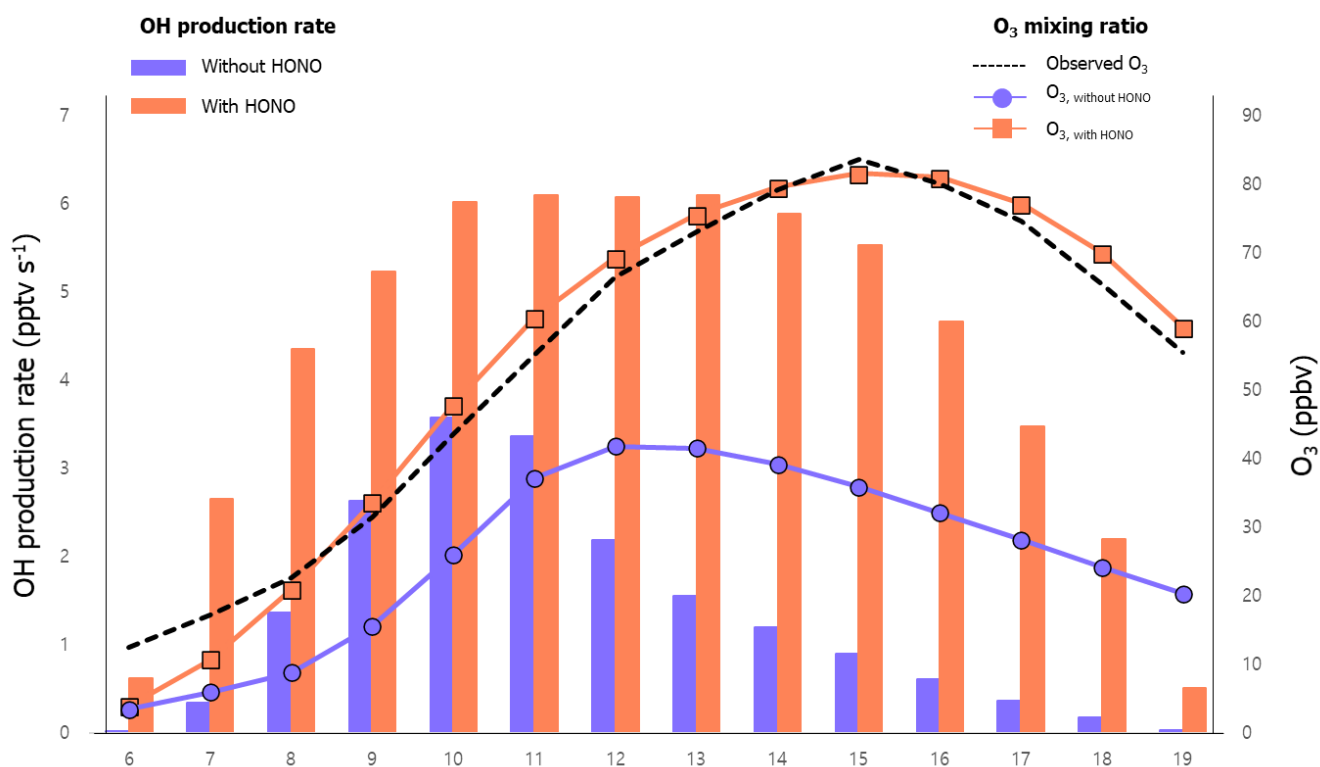
384



385

386 **Figure 7.** Relationship between measured HONO (HONO_{obs}) and modeled HONO (HONO_{mod})
387 using (a) RNDv1.0 and (b) a Random Forest model for the test dataset.

388



390

391 **Figure 8.** For June 2016, diurnal variations of O₃ (line) and OH production rate (bar) calculated
 392 from the F0AM photochemical model with (orange) and without (blue) HONO estimated from
 393 the RNDv1.0 model. The measured O₃ is compared with the calculated.

394

395 **Table 1.** Resources for constructing RND model.

	Version	Remark
Python	v3.8.3	
CUDA	v10.1	*If using GPU
CuDNN	v7.6.5	*If using GPU
Tensorflow	v2.3.0	<i>Python library</i>
Keras	v2.4.3	<i>Python library</i>
Pandas	v1.0.5	<i>Python library</i>
Numpy	v1.18.5	<i>Python library</i>

396

397 *GPU denotes graphic processing unit

398 **Table 2.** Input variables and their concentrations (10th ~ 90th percentile), coverage, and scale
 399 factors for RNDv1.0 model. Measurements were made in Seoul during May ~ June in 2016 and
 400 2019.

	10 th ~90 th percentile (unit)	Coverage (%)	Scale Factor1 (F ₁)*	Scale Factor 2 (F ₂)**
Input Variables				
O ₃	12.1 ~ 90.4 (ppbv)	95.5	204.738	0.842
NO ₂	11.0 ~ 48.6 (ppbv)	80.6	79.925	2.375
CO	252 ~ 743 (ppbv)	95.1	975.248	137.253
SO ₂	1.9 ~ 6.4 (ppbv)	95.6	12.479	0.958
Solar Zenith Angle	22.7 ~ 118.4 (°)	100.0	112.317	14.195
Temperature	15.9 ~ 26.7 (°C)	99.4	24.240	8.610
Relative Humidity	29.2 ~ 79.1 (%)	99.4	88.545	10.555
Wind Speed	0.2 ~ 3.7 (m/s)	99.4	7.581	0.005
Wind Direction	45.4 ~ 287.5 (°)	99.4	359.565	0.235
Output Variables				
HONO	0.3 ~ 2.0 (ppbv)	81.1%	3.447	0.013

401
 402 * Maximum – Minimum
 403 ** Minimum value
 404

405 **Table 3.** The performance of chemical transport model (CMAQv5.3.1) and machine learning
406 (ML) models including Random Forest (RF), Artificial Neural Network (ANN), and RNDv1.0
407 on measurement data from 2016 KORUS-AQ campaign that were used for training.

	CMAQv5.3.1	RF	ANN	RNDv1.0
IOA	0.44	0.99	0.86	0.9
r	-0.07	0.99	0.81	0.84
MAE	0.82	0.1	0.38	0.27
RMSE	1.06	0.12	0.41	0.37

408

409

410 **Table 4.** The result of bootstrap test of measurement data used to train the RF and RNDv1.0
 411 model. The greater the MAE, the greater the influence of variable.

Variable	RF		RNDv1.0	
	MAE	Feature Importance	MAE	Feature Importance
-	0.10	-	0.28	-
O ₃	0.57	1	0.29	8
NO ₂	0.24	4	0.59	1
CO	0.19	7	0.37	5
SO ₂	0.17	8	0.34	6
Solar zenith Angle (SZA)	0.25	2	0.41	4
Temperature (T)	0.21	5	0.52	2
Relative humidity (RH)	0.25	3	0.52	2
Wind speed (WS)	0.20	6	0.34	6
Wind direction (WD)	0.13	9	0.29	8

412

413

414 **Reference**

415

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