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Photochemical aspects of the behavior of the atmospheric radioiodine after the Chernobyl accident

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A hybrid stable iodine/radioiodine (^{131}I) atmospheric photochemistry box model, including 27 reactions, has been developed and solved using algorithmic programme with the application of the Runge-Kutta method of the order 4(5). This modelling offers a clearer view of relationship among aerosol-associated (inorganic iodine compounds, mostly I_2O_2), gaseous inorganic (mostly $IONO_2$, HOI) and organic (CH_3I) iodine compounds in ambient atmosphere. Summing up the data of the Chernobyl accident, the problem of the standardised method for atmospheric aerosol-associated and gaseous (inorganic and organic) radioiodine activity measurements in the case of the nuclear power plant accident is discussed.

Introduction

Over the past decades, rapid progress has been made in understanding the gas-phase photochemical reactions of iodine,[1–3] concerning the chemical and physical processes occurring in the atmosphere. The behavior of iodine in the atmosphere also is of prime consideration to the nuclear industry and is especially important in the case of nuclear accident.

Radioiodine species escaping from ruptured fuel rods are exposed to a strongly reducing, high-temperature containment environment, comprised of steam, as well as other volatilised materials. Radiation effects on such chemical system are quite complex. The iodine compounds CH_3I, HOI and I_2 are found to be the dominant iodine species in the gas phase exhausted to the environment in the case of nuclear accident.[4–8]

The assumption that chemically uncombined elemental iodine was abundant in the atmosphere as well as many other questions, pertaining to iodine behavior in the environment after the Windscale fire, 1957, remain unsolved. It has been shown, that photochemistry of elemental iodine occurs on the rapid time scale and, therefore, the environmental radioiodine behavior must be carefully examined.[2,9]

Following the Chernobyl accident of 1986, the physicochemical compounds of airborne ^{131}I were investigated world-wide. However, the chemical separation of iodine into aerosol-associated, elemental, organic and others as well as relative concentration of each compound were reported only for a few locations. For the most part these data are summarised by KOHLER et al.[10] In the majority of cases only aerosol-associated radioiodine has been determined[11] and estimations for the remaining sites depended on the interpretation of the modeller.

That is why in parallel with laboratory and ambient atmospheric studies, research on photochemical modelling of atmospheric transformations of radioiodine during transport of the radioactive cloud may be performed, as the relevance of stable iodine photochemistry to the behavior of radioiodine is likely to be present.[8,12]

The purpose of this paper is to present a hybrid stable iodine/radioiodine time dependent gas-phase photochemistry box model. The goal of these studies is the elucidation of physicochemical speciation of airborne radioiodine (mainly ^{131}I) after the NPP accident, in the case CH_3I, HOI and I_2 are the main radioiodine compounds released to the post-accident environment.

Model description

A detailed study of the stable iodine cycle and tropospheric photochemistry[8,13–17] testifies that the most easily quantified natural source of the atmospheric stable iodine species is that resulting from the photolysis of CH_3I, HOI and I_2. Gas phase iodine photochemistry in the tropospheric C-N-H-O_3 system has received the most study.[1,2] The necessity of considering the stable iodine cycle in studies of radioiodine resulted from the fact that radioiodine is only a minor component of the atmospheric stable iodine after the NPP accident. For example, during the Windscale fire 0.25 g of ^{131}I was exhausted, during the Chernobyl accident 100 g.

That is why in the first stage the stable iodine time dependent gas-phase photochemistry box model, including 27 photochemical reactions, illustrated schematically in Fig. 1, was under investigation. In this figure circles represent species and arrows connecting circles represent photochemical reactions or mass transport paths connecting the species, with the principal reactants indicated beside the arrows. A complete list of reactions and rate constants is presented in Table 1.

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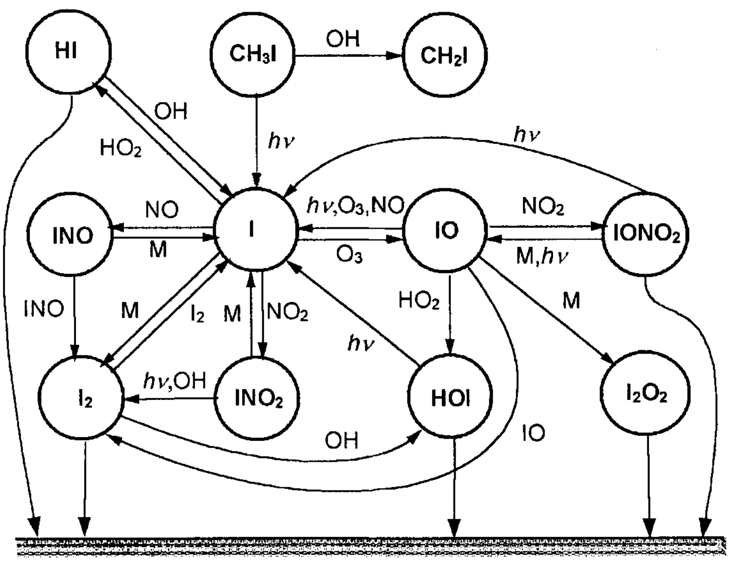

Fig. 1. All-important features of the atmospheric iodine model

Table 1. Kinetic parameters used in numerical simulations

Reaction	Rate[a]
$I_2 + hv \rightarrow I + I$	$5.0 \cdot 10^{-2}$
$IO + hv \rightarrow I + O$	$2.0 \cdot 10^{-1}$
$IONO_2 + hv \rightarrow I + NO_3$	$3.2 \cdot 10^{-3}$
$I + O_3 \rightarrow IO + O_2$	$9.6 \cdot 10^{-13}$
$I + HO_2 \rightarrow HI + O_2$	$3.8 \cdot 10^{-13}$
$I + I + M \rightarrow I_2 + M$	$3.7 \cdot 10^{-32}$
$HI + OH \rightarrow I + H_2O$	$2.5 \cdot 10^{-11}$
$IO + IO \xrightarrow{M} I_2O_2$	$4.0 \cdot 10^{-11}$
$IO + IO \rightarrow 2I + O_2$	$1.0 \cdot 10^{-11}$
$IO + IO \rightarrow I_2 + O_2$	$2.0 \cdot 10^{-12}$
$IO + NO \rightarrow I + NO_2$	$2.0 \cdot 10^{-11}$
$IONO_2 \xrightarrow{M} IO + NO_2$	$5.0 \cdot 10^{-3}$
$I + NO \xrightarrow{M} INO$	$3.4 \cdot 10^{-13b}$
$I + NO_2 \xrightarrow{M} INO_2$	$4.9 \cdot 10^{-12c}$
$IONO_2 + hv \rightarrow IO + NO_2$	$3.2 \cdot 10^{-3}$
$HOI + hv \rightarrow I + OH$	$6.3 \cdot 10^{-3}$
$CH_3I + hv \rightarrow I + CH_3$	$3.0 \cdot 10^{-6}$
$IO + HO_2 \rightarrow HOI + O_2$	$8.2 \cdot 10^{-11}$
$HOI + OH \rightarrow IO + H_2O$	$2.0 \cdot 10^{-13}$
$IO + O_3 \rightarrow I + 2O_2$	$1.0 \cdot 10^{-16}$
$I_2 + OH \rightarrow HOI + I$	$1.8 \cdot 10^{-10}$
$INO + INO \rightarrow I_2 + 2NO$	$1.3 \cdot 10^{-14}$
$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	$4.7 \cdot 10^{-15}$
$CH_3I + OH \rightarrow CH_2I + H_2O$	$7.2 \cdot 10^{-14}$
$IO + NO_2 \xrightarrow{M} IONO_2$	$2.7 \cdot 10^{-12}$
$INO \xrightarrow{M} I + NO$	2.2^{d}
$INO_2 \xrightarrow{M} I + NO_2$	3.9^{e}

[a] Gas-phase reaction rates are in units of s^{-1} for photochemical and one-body reactions, in units of $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for two-body reactions and in units of $cm^6 \cdot molecule^{-2} \cdot s^{-1}$ - for three-body reactions.

[b,c] Reaction rates were evaluated according to TROE[18] with parameter values according ATKINSON et al.:[19] $k_0 = 1.8 \cdot 10^{-32}[N_2]$ $cm^6 \cdot molecule^{-2} \cdot s^{-1}$, $k_\infty = 1.7.10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, $F_c = 0.75$ in [b] case and $k_0 = 3.0 \cdot 10^{-31}[N_2]$ $cm^6 \cdot molecule^{-2} \cdot s^{-1}$, $k_\infty = 6.6.10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, $F_c = 0.63$ in [c] case.

[d,e] Reaction rates were evaluated with regard to the equilibrium constant:[2] $K_{eq} = 10^{-5.7} \exp(9160/T)$ atm^{-1} in [d] case and $K_{eq} = 10^{-6.4} \exp(9560/T)$ atm^{-1} in [e] case.

The rates of the photochemical reactions are taken from References 3, 19–23. The diurnal variation of the photolysis rate was assumed to be proportional to the cosine of the solar zenith angle during the day and zero during the night. This is a reasonable approximation to a clear sky situation.[24,25] This simple scheme should suffice the purpose of testing the numerical scheme. The photolysis rates in most of the tests were calculated for 40°N at equinox. Diurnal temperature variation was not considered and temperature was fixed at 298 K.

The concentration of main tropospheric free radicals and molecular compounds was appropriate for rural continental areas (Table 2). Diurnal course of CH_3I, NO, HO_2 and OH take into account data from GONG et al.[26]

According to JENKIN et al.,[2] deposition of $IONO_2$ and HI was assumed to be $1 \cdot 10^{-5}$ and $2 \cdot 10^{-5}$ s^{-1}, respectively, which that of I_2 $1 \cdot 10^{-5}$ s^{-1}.[9] Aerosol-associated iodine deposition velocity can be about an order of magnitude lower as compared with the above mentioned gaseous species $1 \cdot 10^{-6}$ s^{-1}.[2] Deposition velocity of HOI was assumed to be $5 \cdot 10^{-7}$ s^{-1}.[27]

Table 2. Ambient day and night concentrations used in numerical simulations

Species	Mean concentration, molecule·cm^{-3}	
	Day	Night
O_3	$1.1 \cdot 10^{12}$	$2.7 \cdot 10^{11}$
NO	$5.4 \cdot 10^{9}$	$5.4 \cdot 10^{3}$
NO_2	$2.2 \cdot 10^{10}$	$2.2 \cdot 10^{10}$
HO_2	$2.7 \cdot 10^{8}$	$1.3 \cdot 10^{7}$
OH	$1.0 \cdot 10^{6}$	$1.3 \cdot 10^{4}$

On the basis of the gas phase processes above, in the second stage hybrid stable iodine/radioiodine photochemical cycle kinetic mass balance equations have been solved for each of determining compounds. Numerical solution of a system of the first order ordinary differential equations was made using algorithmic programmes with application of the Runge-Kutta method of the order 4(5).[28]

Results and discussion

Computer simulated diurnal variations of atmospheric stable iodine species with constant CH_3I production rate and concentration (we adopt 2 ppt – typical background concentration for continental atmosphere) under steady state conditions are presented in Fig. 2. This modelling offer a clearer view of temporal relationship among aerosol-associated, gaseous inorganic and organic iodine compounds. As the result of photochemical dissociation of CH_3I the overwhelming bulk of daytime inorganic gaseous iodine species consists of $IONO_2$ together with HOI and aerosol-associated iodine, comprised mostly of I_2O_2. The same result has been obtained in the case of computer simulated diurnal variations of atmospheric stable iodine species in the case of I_2 and HOI photochemical dissociation.

The aerosol-associated radioiodine is likely to be produced by polymerisation of I_2O_2 and possible other inorganic iodine compounds on the surface of background atmospheric aerosol.[2] There is comparative little information on I_2O_2 and $IONO_2$ atmospheric behavior in view of the fact that these compounds are thermally unstable at temperature above 0 °C. Further detailed investigations of aerosol-associated iodine species are clearly required.[3]

The results of computer simulation of the daytime and nighttime release of radioactive $CH_3{}^{131}I$, $^{131}I_2$ and $HO^{131}I$ are presented in Fig. 3. It is evident, that 95% of daytime released $^{131}I_2$ will be photolysed during a very short time, less than one minute as compared with the same of $CH_3{}^{131}I$, 4 days. So any predictions of daytime $^{131}I_2$ (elemental iodine) sampling still remain not clear.

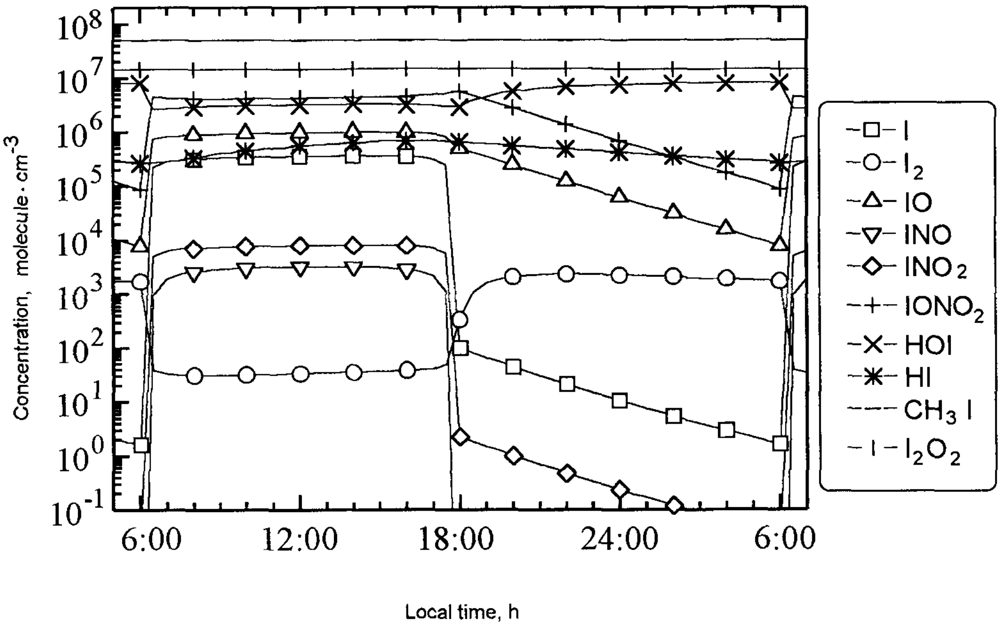

Fig. 2. Calculated diurnal variations of atmospheric iodine species generated as a result of photolytic dissociation of CH_3I under the steady state conditions

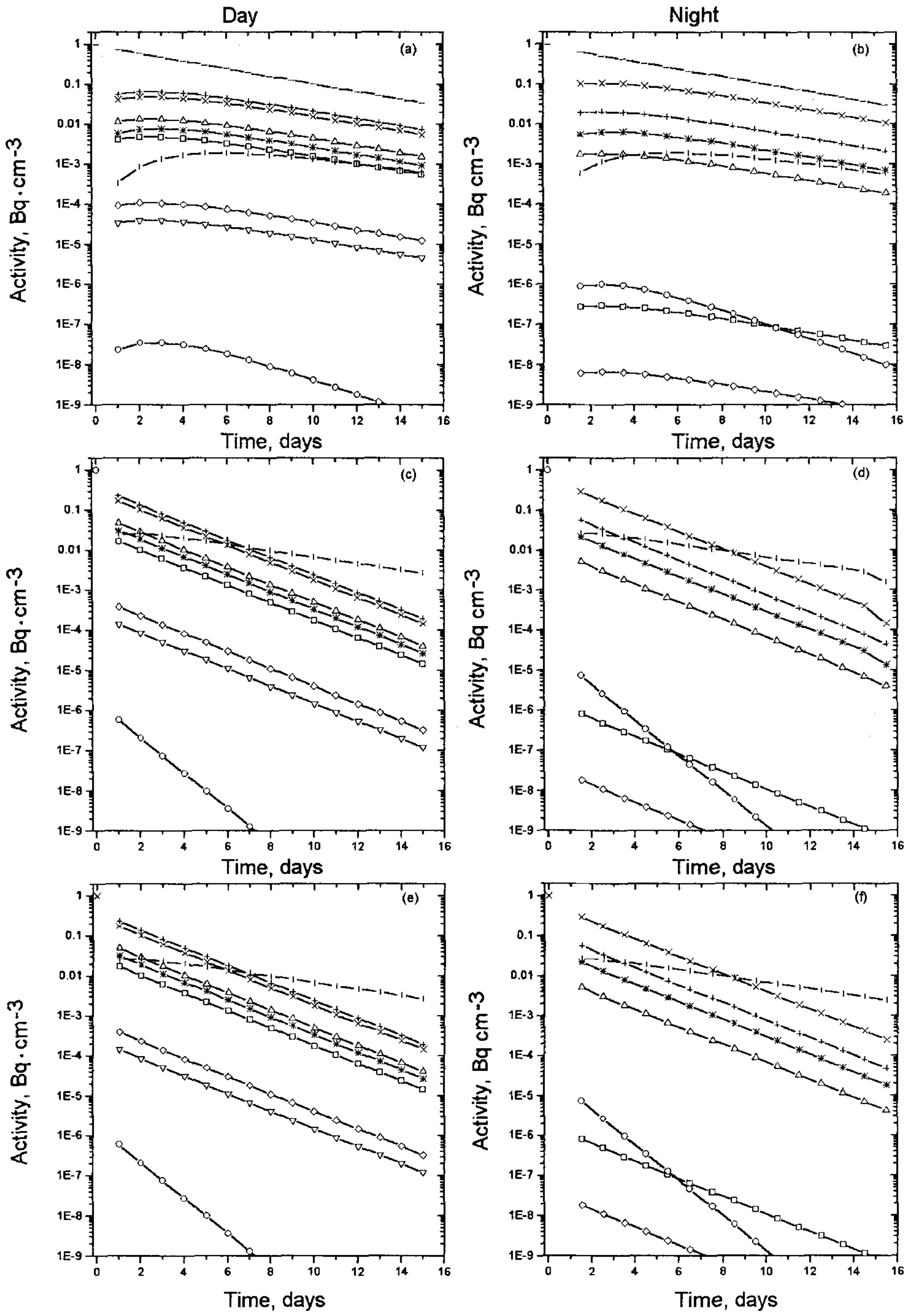

Fig. 3. The temporal daytime and night-time changes of aerosol-associated, gaseous inorganic and gaseous organic ^{131}I species in the case of photodissociation of CH$_3$^{131}I (a,b), ^{131}I$_2$ (c,d) and HO^{131}I (e,f) with initial activity 1 Bq·cm^{-3} for each species

Table 3. The relationship between aerosol-associated, gaseous inorganic and organic radioiodine expressed on a percentage basis and measured after the Chernobyl accident

Aerosol-associated	^{131}I activity, %			Reference
	Elemental	HOI	Organic	
20 ± 3	29 ± 2	–	51 ± 3	KOHLER et al.[10]
19 ± 9	11 ± 5	6 ± 3	70 ± 11	NOGUCHI et al.[12]
35 ± 3	14 ± 2	–	51 ± 2	NEDVECKAITE et al.[29]

The atmospheric concentrations of aerosol-associated or aerosol-associated and gaseous radioiodine from the Chernobyl accident have been studied at a number of sites. However, within the context of this work, we investigate only the special case when aerosol-associated, some compounds of gaseous inorganic and organic iodine was separately measured in ambient atmosphere after the Chernobyl accident. Some results of these measurements are summarised in Table 3. The most unexpected outcome of these measurements were the detection of inorganic and especially organic gaseous ^{131}I in abundance.

As a rule, airborne radioiodine was collected using some kind of aerosol filters for aerosol-associated radioiodine in combination with one or two beds of activated charcoal cartridge for collecting gaseous inorganic iodine compounds and activated charcoal containing 10% triethylenediamine (TEDA) for collecting CH_3I. In specific cases a modified Maypack sampler was used.[12] This sampler separate airborne ^{131}I into four species: (1) particulate iodine, by means of Millipore membrane filter, (2) I_2 by using a set of silver screens, (3) HOI and other inorganic radioiodine compounds by means of charcoal loaded filter paper impregnated by phenol and (4) CH_3I with the help of activated charcoal impregnated with TEDA.

It should be noted that HOI, like CH_3I, penetrates various sorbents including silver surfaces commonly used in atmospheric samplers and thus may explain high organic fractions reported by investigators. Available data indicate that copper zeolite (13x) in the sulphide form is an effective adsorber for HOI and that material does not retain CH_3I.[30] Additional adsorbents need to be developed to provide satisfactory separation of the organic and inorganic gaseous compounds of radioiodine.

That is why post-Chernobyl experimental data of radioiodine activity concentration measurements are unsuitable for comparison in many cases and the nature of the radioiodine compounds can hardly be conceived especially in the case of elemental iodine measurements. Knowledge of ^{131}I compounds abundance, deduced from these computer simulations, supports the evidence for necessity of standardised method for aerosol-associated, gaseous inorganic (mostly $^{131}IONO_2$ and $HO^{131}I$) and organic ($CH_3{}^{131}I$) radioiodine measurements in the case of NPP accidents. These measurements are essential in the field of countermeasures available in an early phase of NPP accidents, thyroid dose assessment as well as in NPP accident scenario's modelling.

This work has been done as an extension of previous work and needs further investigations.

Conclusions

This kinetic modelling attempts to clear up the experimental results of aerosol-associated, gaseous inorganic and organic atmospheric radioiodine activity concentration measurements, that have been performed after the Chernobyl accident. The present results indicated that it is more realistic atmospheric radioiodine compounds called "elemental iodine" to be replaced by "gaseous inorganic radioiodine compounds". It is conceivable that this iodine fraction is mostly comprised of $^{131}IONO_2$ and $HO^{131}I$. It should be particularly emphasized that not much is known about the atmospheric behavior of aerosol-associated and gaseous inorganic iodine species. With respect to the occurrence of various compounds of radioiodine, the collection of samples must be performed in a way enabling the differentiation between aerosol-associated, gaseous inorganic and gaseous organic compounds. The lack of standardised methods for aerosol-associated, inorganic and organic gaseous radioiodine, released during the nuclear power plant accident, is called upon to be solved.

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