POLLUTION SOURCES AND FORMATION OF AIR CONTAMINATION MULTICOMPONENTIAL CONCENTRATION FIELDS OF ORGANIC SUBSTANCES IN NORTH-EASTERN ESTONIA

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The organic compounds from industrial processes have an essential role in the formation of multicomponential concentration fields of pollutants in the overground air layer of North-East Estonian landscapes and dwelling areas. In the towns of Kohtla-Järve and Kiviõli organic compounds form 25-28 % of the total quantity of air pollutants originating from oil shale processing and chemical plants. Among pollutants dominate aliphatic and aromatic hydrocarbons, phenols, formaldehyde, organic dusts, etc. On the basis of special imitation system the calculations of overground maximum and mean concentrations of pollutants, affecting the ecosystems near the oil shale processing plants, were carried out for various areas and territories. The calculating and monitoring data have shown reasonable agreement by testing of imitation system. The results of automatic air monitoring system show that the highest pollutant concentrations occur on the dwelling areas of Kohtla-Järve in calm weather at night before sunrise. The area of essential influence of organic substances to air quality extends to 3-6 km and more from the plants. At Kohtla-Järve the mean daily concentrations exceeded the permissible level for phenol in 9-50 % of all analyses (1991-1994). Some organic pollutants have synergetic toxic effect what is an important factor in assessment of the state of ecosystems.

Introduction

The hydrocarbon composition in the ambient air includes the unburned hydrocarbons from industrial processes and fuels such as gasoline, compounds formed during combustion in the stationary combustion devices and motor vehicles, also natural hydrocarbons emitted by vegetation. Types of organic pollutants present are hydrocarbons (alkanes, alkenes, aromatics), aldehydes, ketones, alcohols, etc. Hydrocarbons emitted from the industrial processes make up approximately 10 % of the total anthropogenic emission rate [1].

Hydrocarbons and other organic substances represent hazardous pollutants the content of which in the air must be controlled as criteria of air quality. These pollutants affect both nature and biota. Several of organic and inorganic compounds such as formaldehyde, phenol, acetone, hexane, nitrogen and sulphur dioxides, ammonia, hydrogen sulphide, etc. have a synergetic toxic effect. This is an important factor on the areas affected with polycomponential pollution [1]. Benzene, formaldehyde, dichloroethane, etc. are suspected carcinogens which are found in urban areas [2]. Hydrocarbons must be controlled also because they are precursors to the toxic photochemical oxidants such as ozone and peroxyacetyl. In this case styrene, aliphatic olefines and aldhehydes, ethers have high reactivity, while ethanol, benzene, acetone, methanol etc. have moderate or low reactivity [2].

Table 1. **Emission of Organic Substances into Air in NE Estonia, t yr⁻¹**

	MPD normative 1990-1991	Factual emission			
		1990	1991	1992	1993
North-Eastern Estonia (total) Including:	15305 (3.3)*1	14451 (3.25)	13495 (3.4)	10603 (3.37)	4622 (1.86)
Kohtla-Järve—Kiviõli area	—	11170 (77.3)*2	10430 (77.2)	8163 (77.0)	3753 (81.2)
OSPA "Põlevkivikeemia"/ / RAS "Kiviter"	7600	7530 (67.4)*3	7454 (71.5)	6538 (80.0)	3377 (89.0)
Kiviõli OSCP/ / RAS "Eesti Kiviõli"	3430	3428 (30.7)*3	2844 (27.3)	1512 (18.5)	332 (8.8)
Aliphatic and aromatic hydrocarbons (NE Estonia)	—	9500 (65.7)*2	9150 (68.0)	7800 (71.7)	3640 (78.8)

F o o t - n o t e : in brackets (for the whole line):
*1 - per cent of the total quantity of air pollutants in NE Estonia;
*2 - per cent of the organic pollutants in NE Estonia;
*3 - per sent of the organic pollutants in Kohtla-Järve—Kiviõli area.

The landscapes and residential areas of North-Eastern (NE) Estonia are affected by all forms of atmospheric pollution, such as hazardous gases, solid particles and aerosols. Besides oil shale fly ash and sulphur dioxide emitted with flue gases from stacks of the Estonian, Baltic, Kohtla-Järve and Ahtme power plants in quantities totalling about 90 % of all pollutants released into atmosphere by stationary sources in NE Estonia, the organic substances from industrial processes play an essential role in the formation of multicomponent concentration fields in the overground air layer. The oil shale processing and chemical plants at Kohtla-Järve and Kiviõli as well as building materials factories and other enterprises of this locality are producing about 77-81 % (Table 1) of NE Estonian organic air pollutants.

In the atmosphere the pollutants are subject to spreading and dispersion. Those processes are complicated and the structure of the overground concentration fields and the pollution level depend on various

factors such as the height of the source, the parameters of emission intensity, meteorological characteristics, chemical reactions in the atmosphere, surface profile, distance from source to given point or area etc. It is general that for assessing hazardous effect of pollutants to environment, especially to air quality, the next two main criteria are used: the momentary maximum concentration (i.e. the maximally possible concentration of pollutant measured per 20-30 min.) and the average concentration for a longer period, such as a day, month, quarter, year, etc. In practice by those criteria the permissible limit concentrations of chemicals are regulated in the atmosphere of residential areas and with regard to protection of flora.

The air quality is usually determined by stationary monitoring stations or by modelling of the pollutants dispersion by means of special computer--based calculation programs. At present the only automation system "Opsis" in NE Estonia (also in Estonia) is in operation at Kohtla-Järve which enables monitoring of organic substances in the atmosphere [3]. For estimating the air quality in the dwelling and natural areas of other regions, also with respect to a large number of pollutants (aliphatic hydrocarbons, hexene, ethylbenzene, dichloroethane, methanol, organic dusts, etc.) nonregistered by "Opsis", we have developed a mathematical imitation system for assessment and forecasting of the air pollution level as one component of the state of environment.

In this article the main results of investigations of pollution sources and formation of air pollution level are given. Also the study and assessment of the air quality by air monitoring and modelling with the aid of special imitation system of organic pollutants dispersion has been carried out, especially for the Kohtla-Järve—Kiviõli area. This is the first exhaustive review and study in this particular field of air pollution problems in Estonia.

Organic Pollutants and Pollution Sources

1. Location of Sources and the Amounts of Pollutants

In the Regional Data Bank of NE Estonian Air Pollution Sources compiled by the Institute of Ecology [4-6] about 580 stationary points, linear and area-type pollution sources which emit organic substances into air are registered.

A more detailed inventory of the stationary pollution sources was carried out in 1990 [7]. As a result of these investigations about 4500 t yr^{-1} of aliphatic and aromatic hydrocarbons emitted and not recorded in the official annual reports of enterprises were fixed and taken into account additionally. For the Kohtla-Järve Oil Shale Processing Association (OSPA) "Põlevkivikeemia" (at present RAS "Kiviter" and the Kiviõli Oil Shale Chemical Plant (OSCP, at present RAS "Eesti Kiviõli") the Maximum Permissible Discharges (MPD) were limited on the level of 11,030 t yr^{-1} of organic pollutants (Table 1).

Table 2. The Annual Emission of Individual Organic Substances on the Kohtla-Järve and Kiviõli Area (Statistical Data)

| Pollutants | OSPA "Põlevkivikeemia" / RAS "Kiviter" | | | | | | | Kohtla-Järve and Kiviõli region | | | |
| | Amount, t | | | | 1995-1996 (MPD) | Intensity, g s⁻¹ | | Amount, t | | | |
	1990	1991	1992	1993		1990	1995 (MPD)	1990	1991	1992	1993
Formaldehyde	2.8	2.8	2.4	0.2	2.5	0.1	0.1	128.3	109.1	24.6	5.4
Phenols	11.7	11.6	9.7	5.8	14	0.5	0.7-1.1	50.9	45.7	17.6	6.6
Methanol	16.8	16.8	13.7	–	3.9	2.4	0.6	203	203	116	125
Hydrocarbons:											
Aliphatic*1	4205	4200	3838	2069	4588*2	284	231-262*2	6456	6052	4969	2354
Benzene	1803	1803	1662	811	879	83	54-86	1803	1850	1682	811
Toluene	624	624	579	290	250	32	16-19	995	894	701	314
Xylene	–	–	–	–	6.8	–	0.3-0.7	–	–	–	–
Styrene	11.6	11.6	10	5.2	22	0.5	1.0-1.5	135	102	49	11.8
Ethylbenzene	–	1.7	1.8	–	5.2	0.1	0.2-0.4	339	206	103	3.6
Dusts:											
Urea*3	841	758	398	153	1158	32	46.4	841	758	398	153
Detergents	–	–	–	–	–	1.5	–	148	148	38.3	16
Others (ethers, acetates, alcohols, acetone, etc.)	14.1	24.5	23.4	42.8	25.6	–	–	69.8	62.2	64.5	65.5
Total :	7530	7453	6538	3377	6955	–	–	11170	10430	8163	3753

*1 Including the light fraction (gasoline) of shale oil.
*2 Including 815 t (41 g s⁻¹) of hexene + heptene and 524.2 t (25-50 g s⁻¹) of hexane + pentane.
*3 Together with AS Nitrofert (mineral fertilizer production), in 1995-1996 about 1155 t of urea.

Table 3. The Content of Pollutants in the Atmosphere of Kohtla-Järve by OPSIS Air Monitoring Data, mg m⁻³

Concentrations	Year	Sulphur dioxide	Nitrogen dioxide	Benzene	Toluene	Formaldehyde	Phenol	Styrene
The Permissible Limit Concentrations (PLC):								
Per 30 min. (MPLC)	—	500	80(100)*1	1500(200)*1	600(200)*1	35(100)*1	10(50)*1	40
Mean per day (24 h)	—	50	40	100(200)*1	600(200)*1	10(50)*1	3	2
Number of analyses	1991	32575	35575	21070	21682	20210	14142	2400
	1992	15155	19112	9717	8250	11511	7149	2894
	1993	12617	15051	3978	9985	11046	4498	1165
	1994*3	13255	11554	4218	3819	3567	3302	1534
Maximum concentration per 30 min.	1991	442	118(0.1)*2	569	3100(0.5)	30	158(10.5)	47(0.01)
	1992	342	85(0.01)	562	495	65(0.07)	82(2.6)	36
	1993	348	84	194	611	20	23(1.5)	34
	1994	271	87(0.02)	316	469	15	23(1.6)	56(0.01)
Maximum concentration per 30 min. at 95 % probability	1991	71	29	66	106	5.5	16	7.5
	1992	64	22	54	63	6.2	7	7.9
	1993	77	23	37	37	5.6	5.5	7
Mean concentration per 24 h (maximum values)	1991	108(6)	62(2)	98	363	5.3	32 (50)	10.4(65)
	1992	106(6)	27	143(0.5)	85	11.1(0.5)	24.7(36)	12.8(75)
	1993	113(7)	35	43	118	5.7	6.6(10)	17.6(51)
	1994	73(3)	29	98	74	11.4(0.7)	24.1(9)	9.4(17)
Annual mean concentration	1991	19	10	20	36	2.3	4.7	2.6
	1992	16	10	19	19	2.8	2.8	3.1
	1993	17	9.7	18	14	2.3	1.8	2.3
	1994	12	8.7	17	18	2.7	2.0	1.4

*1 In brackets the new norms of PLC valid from January 1, 1995 are shown.
*2 The per cent of PLC exeeded values, %.
*3 In 1994 for organic compounds by data from September to December only.

In reality, MPD is the environmental protection standard, limiting the maximum quantity per year (t yr^{-1}) and maximum emission intensity per second (g s^{-1}) for owners of the pollution sources in accordance with which they are allowed to emit pollutants without special sanctions. Since the computer-based calculations of pollutants dispersion in the air showed that the concentrations of phenols, formaldehyde, styrene, ethylbenzene and light gasoline fraction of shale oil exceed 3.5-12.5 times the Maximum Permissible Limit Concentration (MPLC) in the atmospheric air of dwelling areas in Kohtla-Järve and Kiviõli regions, the MPD limits for those contaminants were approved as temporary for 3-5 years.

Table 1 shows that the share of organic compounds in total air pollutants in NE Estonia is approximately 3.2-3.4 % (in 1990-1992 about 10,600-14,450 t). On the areas of the towns of Kohtla-Järve and Kiviõli the relative significance of those compounds is essentially higher (25-28 %) [9].

In Table 2 data are given about the actual annual amounts and maximum emission intensity of hazardous organic compounds released according to official reports of enterprises into the air in the Kohtla-Järve—Kiviõli industrial area, and the respective MPD. Data for RAS "Kiviter" as the main producer of pollutants are given separately.

Compared to 1990-1991 the emission of organic substances from sources of RAS "Kiviter" was reduced by 13-55 % during the period of 1992-1993 (Table 2) since a number of environmentally hazardous manufacturing processes were closed down as a result of a decrease in the capacity of production and economic difficulties. The reduction was especially great in RAS "Eesti Kiviõli" where during the period of 1990-1993 the production of formaline, detergents and "Kukersol" dropped from year to year. The result was that in comparison with the total annual quantity of organic emissions in 1990-1991 (60-70 t of formaldehyde, 1800-2160 t of aliphatic hydrocarbons, 200 t of methanol, 250-350 t of toluene, 90-123 t of styrene, 339 t of ethylbenzene, 148 t of alkylsulphates etc.) only about 10 % was emitted from stationary sources of RAS "Eesti Kiviõli" in 1993 (332 t, see Table 1).

This tendency is characteristic of all organic emissions taking place in NE Estonia (Table 1). However, the reduction is of temporary character and the economic growth will again cause an increase in the discharges and in the pollution level. For example, according to the MPD limits for RAS "Kiviter", which were worked out by the Institute of Ecology in 1994 and are valid from the beginning of 1995, the annual amount of organic pollutants will be up to 5800 t (approximately the level of 1992) and the maximum emission intensity for contaminants will be limited, g s^{-1}: aliphatic hydrocarbons - 231-262, benzene - 54-86, toluene - 16-19, phenols - 0.7-1.1 etc. (Table 2).

At the same time, the pollution of atmosphere with organic substances on the Kohtla-Järve-Kiviõli area is caused to the extent of 98 % (Table 1) by the local oil shale processing and chemical plants. The remaining part of the pollutants are emitted from mineral wool, furniture, wood particle board and other productions.

Among other NE Estonian pollution sources Sillamäe Metallurgy and Chemistry Plant (at present RAS "Silmet") should be mentioned, where in 1990-1991 from the production of filter materials about 3000 t yr^{-1} (in 1993-344 t) of dichloroethane was emitted. The discharges of hydrocarbons from oil shale processing by the solid heat carrier method (at the Estonian TPP) were fixed in 1990-1991 at the level 67-83 t yr^{-1}, and in 1993 up to 361 t. In the town of Narva the main sources of organic emissions are located in the chrome-leather and furniture factories (in 1993-1994 about 100 t yr^{-1} of ethyl- and butylacetate, toluene etc. was discharged).

2. Share of Organic Pollutants

In the atmosphere of Kohtla-Järve and Kiviõli and its surroundings altogether over 30 different organic substances have been detected for which the Permissible Limit Concentrations (PLC - the maximum value per 30 min and mean per day) for atmospheric air of dwelling areas are established in Estonia, therewith the sum of aliphatic hydrocarbons is regarded as one component [4].

The majority of the components emitted are hydrocarbons totalling 66-79 % of organic pollutants in NE Estonia (Table 1). In Kohtla-Järve and Kiviõli region the role of aliphatic compounds is 58-63 % and that of aromatic - 29-31 %, urea - 6.6 %, methanol - 2 %, formaldehyde -1 %, phenol - 0.4 %, etc. (1991-1993). It can be seen in Table 2 that accordingly in the MPD norms of 1995 for organic discharges from RAS "Kiviter" the share of aliphatic hydrocarbons is up to 79 % (hexene + + heptene - 14 %), benzene - 15.1 %, toluene - 4.3 %, phenol - 0.25 %, etc. At RAS "Kiviter" about 61 % of organics are emitted from oil shale processing equipment and 37 % from processing of imported petroleum derived pyrolysis oil (the production of aromatic hydrocarbons), the rest comes from the benzoic acid and synthetic resins production, etc.

The largest sources of hydrocarbons are the coke-ash dumps in the neighbourhood of the RAS "Kiviter" where annually about 135,000 t of liquid residues, containing as much as 1.3-1.9 % of gasoline fraction and 1.1-1.5 % of shale oil, are pumped or transported to those dumps. There are pumped also about 30,900 m^3 per day of technological waste waters which contain about 7.4 mg l^{-1} of volatile phenols, but their role in air pollution has not been studied so far.

Besides coke-ash dumps, technological equipment and ventilation systems there are numerous other sources of emission of organic compounds such as storage of liquid products and raw materials, tanks, filling and pumping out operations in tank cars, sewage systems, etc. At present, compared with modern oil processing plants, the discharge intensity of liquid products vapours from oil shale processing installations is relatively high caused by large number (60 %) of small-capacity vessels, 100 to 200 m^3 and below. The maximum discharge intensity from tanks and vessels of light products at their temperature 30-40 °C in the warm and 15-25 °C in the cold season period lying in the following ranges (kg per cubic metre of pumped product): for benzene - 1.1-1.3; toluene - 0.3-
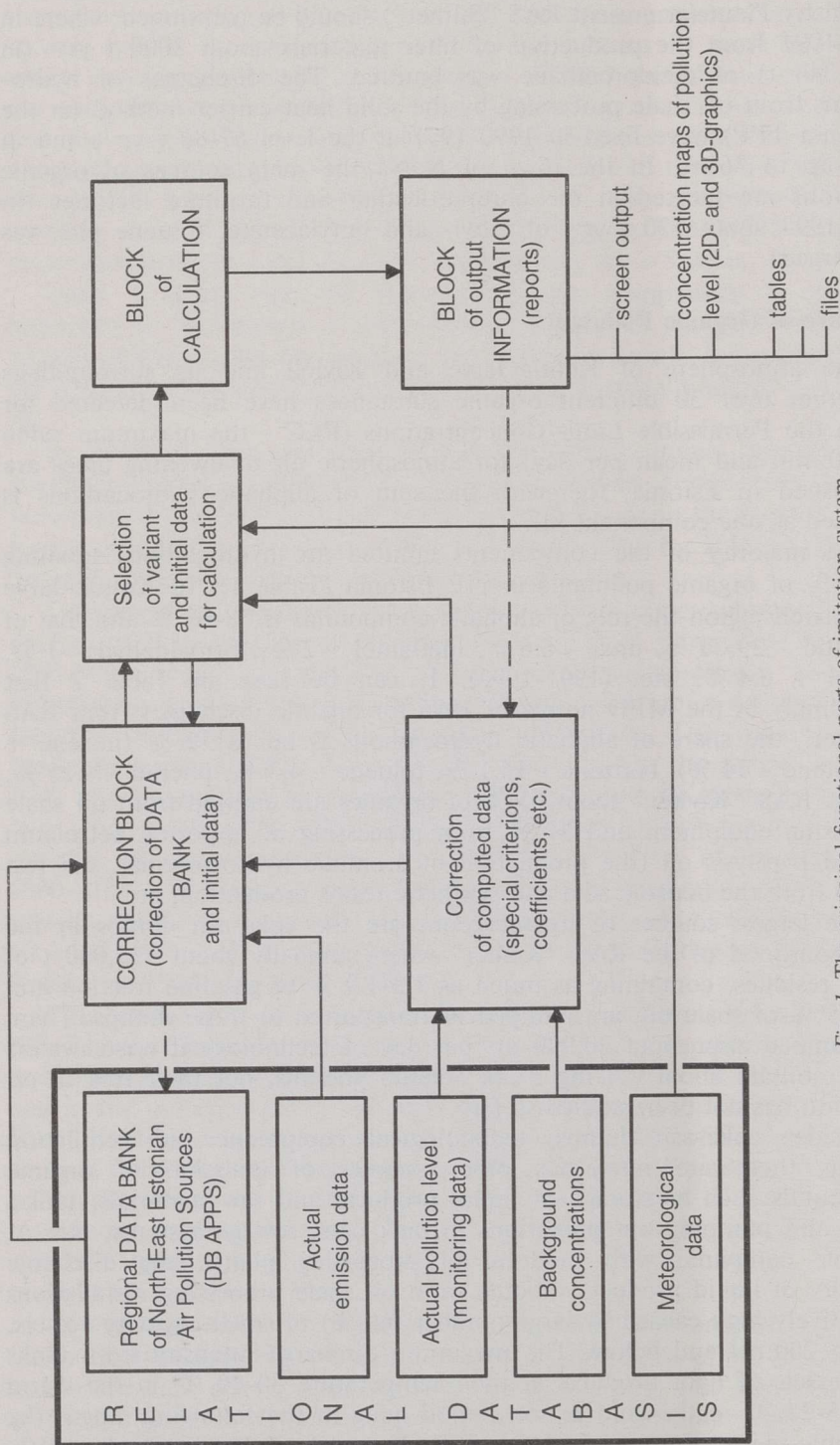
Fig. 1. The principal functional parts of imitation system for assessment of the air pollution level

Table 4. **Maximum Concentrations of Pollutants in the Atmosphere of Settlements and Dwelling Areas Near RAS "Kiviter" by Critical Wind Directions, mg m^{-3}**

Names	Kohtla-Järve		Käva	Saka-Ontika region		Aa	Kohtla-Nõmme
	Centre						
	(1)	(2)	(1)	(1)	(3)	(1)	(1)
Critical wind direction:							
Rhumb		SW,W	NO,N		S,SW	SO	NO
Repetition of wind rhumb, %		34-44	5-18		134-45	7-10	7-8
Distance from main pollution sources, km		2-3	1-1.5	2-3		6-7	2.5-3
Organic pollutants:							
Benzene	150-350	357 / 43-119	450-700	150-290	—	150	750
Toluene	60-195	465(W) / 44-448	120-200	60-125	—	60	235
Styrene	2-6	30(W) / 7-9	6-10	—	3-13 / 15-21	7.5	—
Phenol	6-12	56 / 6-25	9-16	6-9	7-23 / 19-38	8	10-16
Formaldehyde	14-20	12(SW) / 4-6	13	10-14	130-1470*	500	32
Aliphatic hydrocarbons	700-1800	—	1400-3000	600-1030	—	—	1300
Incl. hexene,heptene	140-360	—	280-600	—	—	—	—
Buthylacetate	5	—	5-10	—	—	—	—
Methanol	10-50	—	50-75	—	—	—	—
Inorganic pollutants:							
Sulphur dioxide	200-350	282(SW) / 120-147	250-400	200-300	60-523 / 318-730	240	200
Nitrogen dioxide	60-65	59(SW) / 14-30	65-70	70-80	30-110 / 150-220	65	75
Carbon monoxide	2700	—	2700	2400-4000	—	2500	2500
Hydrogen sulphide	5.6-7.2	—	7.2-8.8	7-12	2-18 / 19-28	8.8	24
Ammonia	160-190	34(1994)	160-180	160-190	30-290 / 80-410	180	170

F o o t - n o t e s : (1) calculated data;
(2) "Opsis"-monitoring data (1991-1993): average of maximums/interval of maximums at 95 % probability;
(3) special investigations in spring (march-may) of 1994: by wind velosity 1-6 m s⁻¹ / 0.2-0.6 m s⁻¹.
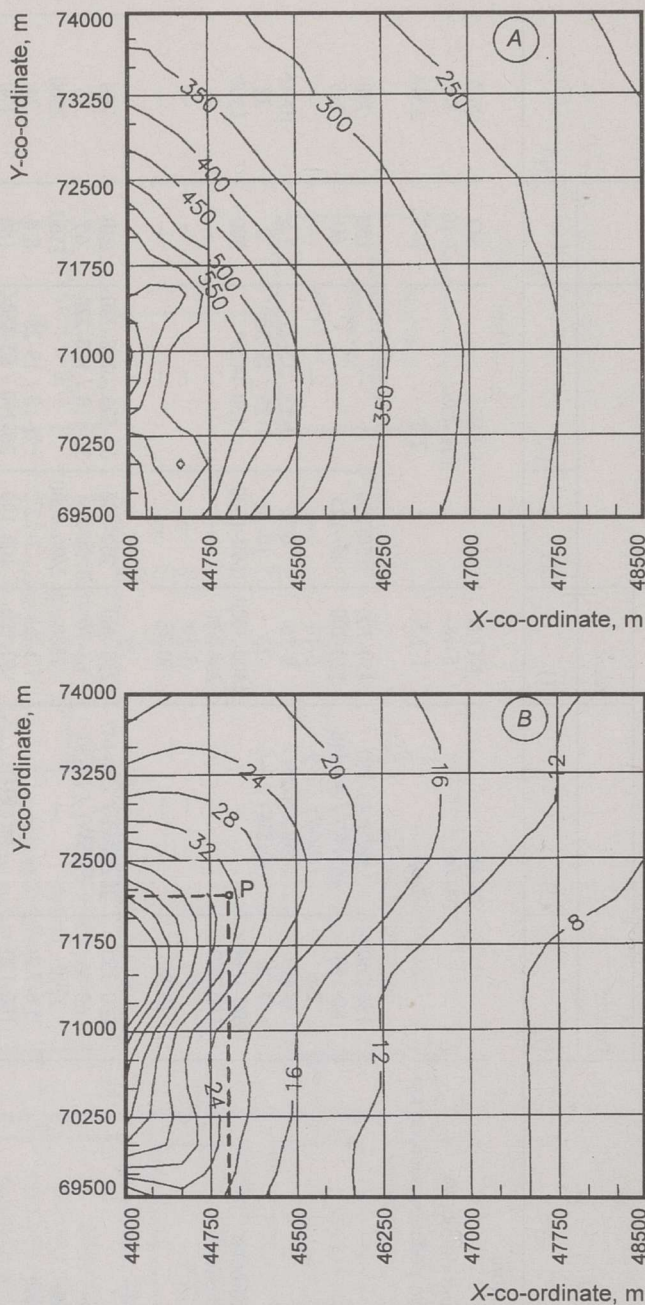* The hydrocarbons of total.

Fig. 2. The isoconcentration fields (μg m^{-3}) of toluene in Kohtla-Järve region:
A - maximum short-time concentrations (MC) of toluene by maximum intensity of
emission 33.4 g s^{-1} (27 sources) and air temperature 19.8 °C;
B - yearly mean concentration (C_{kp}) by wind rose, %: N - 8.0; NO - 7.4; O - 6.9;
SO - 6.8; S - 13.1; SW - 29.6; W - 13.7; and, NW - 14.5; wind velocity - 3.2-
-4.7 m s^{-1}; mean emission intensity - 23.1 g s^{-1}, mean air temperature -7.9 °C

Wind direction		$C_{kr,f}$,
Rhumb	Degrees	$\mu g\ m^{-3}$
N	338-22	14.84
NO	23-67	13.93
O	68-112	13.96
SO	113-157	13.93
S	158-202	14.35
SW	203-247	78.21
W	248-292	18.71
NW	293-337	14.45
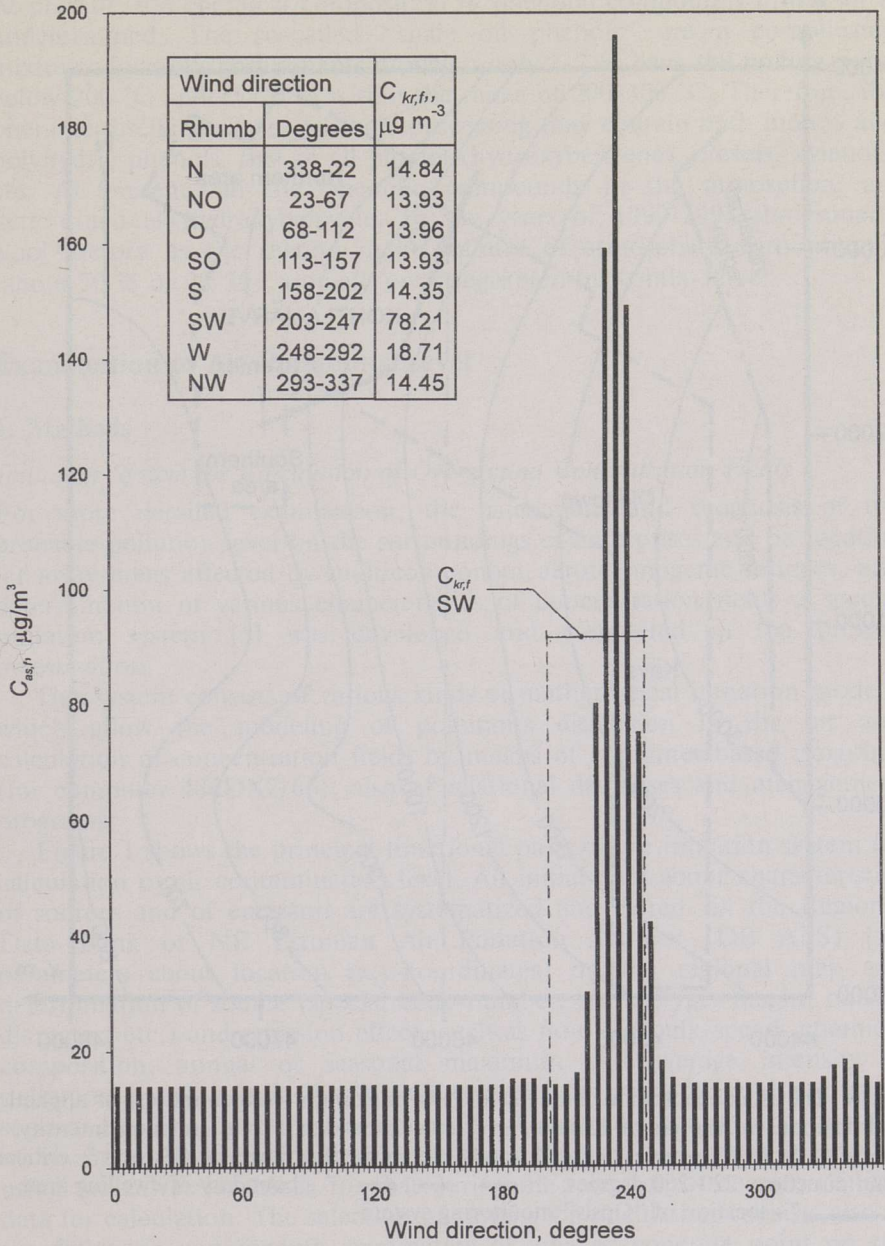
Fig. 3. The annual mean concentrations of toluene dependent on the wind directions and mean values for wind rhumbs ($C_{kr,\ f}$) on the point P with coordinates $X = 44900$ m and $Y = 72200$ m (Fig. 2,B): the mean concentration C_{kp} in given point P - 33.82 $\mu g\ m^{-3}$; $F_k = 70\ \%$
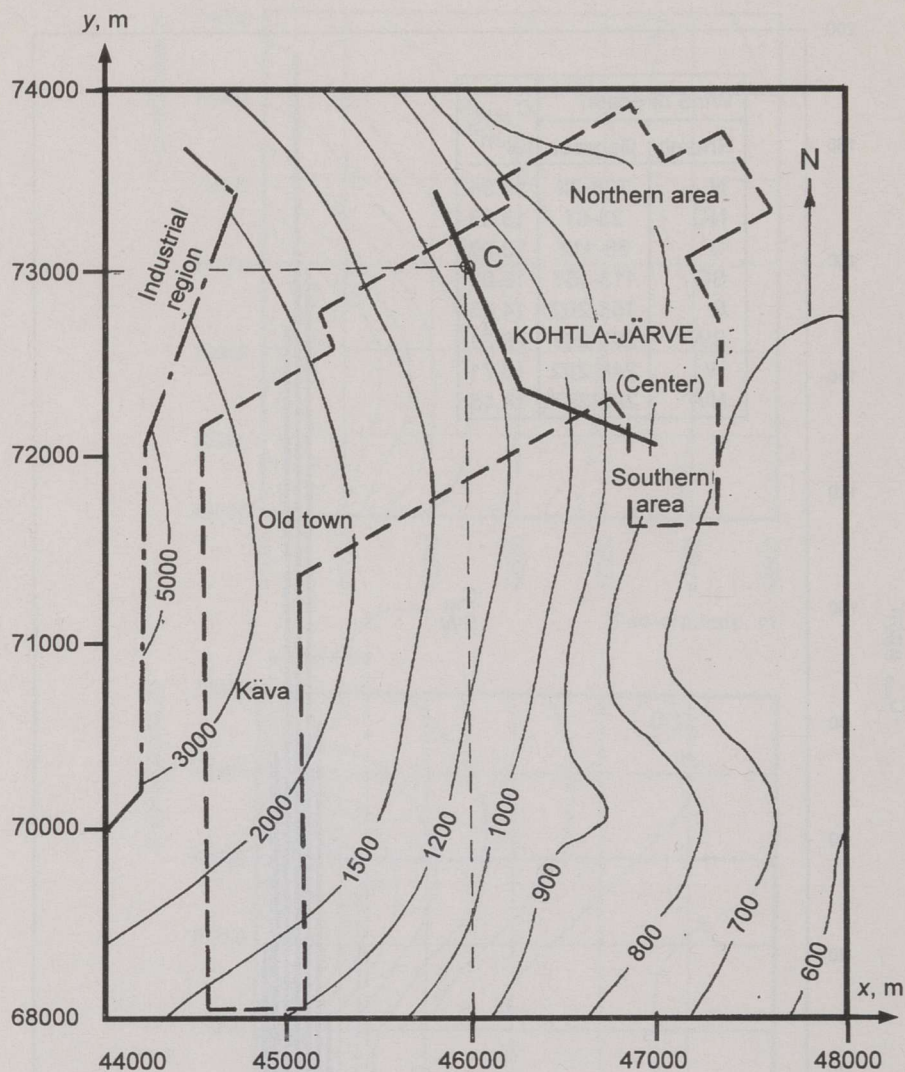
Fig. 4. The isoconcentration lines (μg m^{-3}) of maximum concentrations of aliphatic hydrocarbons in the air of Kohtla-Järve (calculated data): total emission intensity - 215 g s^{-1} from 82 sources; critical wind velocity in the range of 4-9 m s^{-1}; critical wind directions 220-260 degrees; " ▬ ▬ ▬ " - boundary of dwelling area; " ▬▬▬ " - location of "Opsis" monitoring system

0.45; gasoline fraction of shale oil - 0.6-1.1; top fraction of pyrolysis oil - up to 4.3 [10]. The losses of crude shale oil are lower and they are in average 0.001-0.006 kg t^{-1} for heavy oil (at 80-100 °C) and 0.15-0.49 kg t^{-1} for light-middle oil (40-70 °C).

One of the more specific pollutants in oil shale processing are the phenols, which are emitted from low sources (more 80) and for that reason dispersion of those components in the atmosphere is relatively bad.

At present, the chemical composition of phenolic compounds in the air is undetermined. The so-called "shale oil phenols" are a complicated mixture of various components of which only 3-7 % have the boiling point below 200 °C and 15-20 % within the range of 200-300 °C. Therefore, the phenolic discharges from oil shale processing may contain both mono- and polyhydric phenols, first of all phenol (hydroxybenzene), cresols, xylenols, etc. At present, all the phenolic compounds in the atmosphere are determined as hydroxybenzene. In the years of 1990-1991 the mineral wool factory as the second main polluter of atmosphere with phenols (about 70 % or 28-30 t annually) was registered in Kohtla-Järve.

Examination of Air Pollutants Level

1. Methods

Imitation System for Calculation of Overground Concentration Fields

For more detailed examination, the assessment and prognosis of the probable pollution level on the surroundings of enterprises and on locating far away areas affected by multicomponent aerotechnogenic influxes, and determination of various characteristics of concentration fields a special imitation system [5] was developed and completed in the present investigation.

This system consists of various kinds of mathematical imitation models, which allow the modeling of pollutants dispersion in the air and calculation of concentration fields by means of computer-based programs (for computer 486DX2/66), also of relational databases and management programs.

Figure 1 shows the principal functional parts of the imitation system for calculation of air contamination level. All initial data about characteristics of sources and of emission are systematized and stored in the Regional Data Bank of NE Estonian Air Pollution Sources (DB APS) [5]: parameters about location (x,y-coordinates) on the regional map and determination of source (special code-number, name, type, height, out-let diameter, etc.) and emission effect, such as flow-out bulk-speed, chemical composition, annual or seasonal maximum and average intensity of pollutants per time unit (g s^{-1}), total quantity per year, for cold and warm season, etc. The operative correction of data about intensity and quantity of discharges by actual emission data reported by enterprises is possible using the correction-block for that during the selection of necessary initial data for calculation. The selection of variant for calculation consists also of the following components: parameters of area or concrete point on the landscape for which the calculations would be carried out, values of the background pollutants, meteorological data (wind rose, wind direction and velocity, temperature), coefficient of atmospheric temperature stratification etc.

In the block of calculation(Fig. 1) the numerical semi-empirical modelling method (OND-86) [8], developed by the Main Geophysical Observatory (St.-Petersburg, Russia) and realized by unified packets of computer programs, is used as the base method. Calculations may be

carried out for different territories, while for every *x-y* coordinates network point with an interval of 0.1 up to over 2 km the maximum (MC, mg m^{-3}) and mean concentrations, and the critical direction and velocity of the wind in that point, at which MC values formed by the time, and the simultaneous influence of all the sources have been taken into account in the modelling of the pollutants dispersion. In addition, the major sources of discharge having cardinal importance in formation of the pollution level would be determined. The results of calculation (the packets of output data) are obtained in the forms of tables, 3D-graphics, and maps (Figs 2 and 4), in which the isoconcentration lines are presented.

Calculation of the Mean Concentration Fields

Concentration maps of MC fields characterize a short-time maximum pollution level with 95 % probability that may be formed by critical wind parameters mentioned above in a given point of the landscapes and dwelling areas. The mean concentrations of pollutant per year, quarter, month, season or another period in given locality of landscape are different from MC values, since the mean values of concentration fields essentially depend on factual distribution of wind directions (wind rose) during the observable period, also on the location of sources with respect to a given point, and on average emission intensity. The territories situated in the leeward direction from the major polluters are polluted to a greater extent. Also, distribution of winds on the various areas is different. For example, in Jõhvi area the south-west winds dominate on the level of 19 % per year, while in Kohtla-Järve this wind direction forms 26-30 % (1991-1992).

Whereas the mean level of air contamination is an important indicator for assessment of the state of atmosphere and ecosystems, corresponding calculation method by modifying of the base program was elaborated. This is based on using the average emission intensity values per given period, also mean air temperature and actual distribution of wind direction and velocity.

For calculation of mean concentrations the general concentration field (obtained by calculation of pollutants dispersion) of the pollutant divided into eight wind rhumbs (parts) according to the wind rose (N, NO, O, SO, S, SW, W, NW) and the mean value for each rhumb on the basis of nine wind directions in this rhumb (after each five degrees) were determined. In case of uniform distribution of the wind within the rhumb, the mean concentration C_{kp} of the pollutant in the overground air layer in a given point of landscape at concrete wind velocity is calculated by formulas:

$$C_{kp} = \sum_{q=1}^{R} C_{kr,q} * S_{r,q} * 10^{-2} \tag{1}$$

$$C_{kr} = \frac{\sum_{m=1}^{D} C_{as,m}}{D} \tag{2}$$

$$C_{as} = \sum_{i=1}^{N} C_{a,i}$$

$$(3)$$

where C_{kr} - the mean concentration for concrete wind rhumb;

S_r - repetition of the wind rhumb per given period (accordingly to wind rose), %;

C_{as} - total of pollutant concentrations caused by individual sources affecting the given point at concrete wind direction;

C_a - concentration of the pollutant in the given point caused by the individual pollution source (by average emission intensity);

q - the number of wind rhumbs ($R = 8$);

i - the number of individual pollution sources affecting the given point;

m - the number of wind directions which are taken into account within each wind rhumb (if after each 5 degrees then $D = 9$).

Analysis of the air pollution level showed that there were differences between monitoring data (actual pollution level) and calculated mean concentrations. This is caused by up to now unknown and unaccounted local pollution sources (for example, in case of nitrogen oxides the emission from nonstationary sources such as motor vehicles), unstable character of wind directions, nonlinear spreading and dispersion of pollutants on the distance from the source to a given point of landscape, etc. As a result the so-called "local background pollution level" is formed which influences the actual pollution level. For consideration of this effect, on the basis of comparison of the Opsis-system data during the last four years with calculated pollution levels and analysis by factor- and multiregression methods, the special coefficient F_k was worked out. It is especially essential to use this coefficient in case of lower sources such as area-type sources of benzene, toluene, phenol etc. The factual mean concentration $C_{kr,f}$ for the given wind rhumb can be calculated by formula:

$$C_{kr,f} = \frac{100\ C_{kr} + C_{kp}\ F_k}{100 + F_k}$$

$$(4)$$

Analogically the values of C_{as} can be corrected.

Values of F_k depend, first of all, on height and type of the pollution source. In NE Estonia, for stacks of power plants and boiler houses $F_k = 20$ % approximately, for lower sources (reservoirs and tanks of liquid products) $F_k = 60\text{-}80$ %. Actually, F_k shows this part of the calculated C_{kp} value which must be redivided between different wind directions in calculation of the mean concentration for a concrete wind rhumb.

For example, in Fig. 2 results of computation of maximum and mean concentrations for toluene in Kohtla-Järve area (x,y axes show the coordinates on the regional map, m - see also Fig. 4) are shown. The number of pollution sources (about 27 from RAS "Kiviter") taken into account in both calculations is constant, and so is the mean emission intensity.

The short-time maximum concentrations (Fig. 2A) on this area formed at critical wind velocity of 0.6-1.4 m s^{-1} and critical wind direction in the ranges of 202-305 degrees (SW and W side winds).

Figures 2B and 3 demonstrate the annual mean concentrations of toluene at different points of the given area dependent on wind directions. We can see that the given point of the landscape (Fig. 3, point P: X = = 44900 m and Y = 72250 m) is directly affected by⁻ toluene contamination by south-western (wind rhumb 203-247 degrees N) winds. The annual mean (C_{kp}) concentration, taking into account all wind directions, is 33.8 mg m^{-3}, the $C_{as,f}$ values lying in the ranges of 13.9-195.8 mg m^{-3} and the annual mean concentration $C_{kr,f}$ for this wind rhumb is 78.2 mg m^{-3}. In this example C_{kr} = 109.3 mg m^{-3}. The difference between C_{kr} and $C_{kr,f}$, i.e. 31.1 mg m^{-3} shows this part of concentration by which the factual mean concentration for the wind rhumb is lower than the calculated mean concentration due to the nonlinear wind direction and the dispersion of pollutants (in some other cases it would be $C_{kr,f} > C_{kp}$).

2. Results and Discussion

For study of the multicomponential structure and dynamics of formation of air pollution fields the data obtained by above described imitation system and air monitoring were used.

Automatic Air Monitoring in Kohtla-Järve

The Opsis-system (Swedish company "Opsis") for continuous monitoring of gaseous components was set up in Kohtla-Järve in December 1990. It is located at a distance of 2-3 km from the oil shale processing plant (RAS "Kiviter") and has three measuring lines each 300-1200 m long (Fig. 4). This automatic monitoring station enables at present continuous recording of five organic substances - benzene, toluene, styrene, phenol and formaldehyde, and, in addition to them also that of sulphur and nitrogen dioxides, nitrogen oxide and ammonia which form with organic contaminants the groups of synergetic toxic effect.

The main results of air monitoring are given in Table 3. In 1991-1994 the maximum concentrations per 30 min. exceeded the LPC level for phenol in 1.5-10.5 % of cases of all analysis. The mean concentrations per day exceeded the LPC for phenol in 9-50 % of cases and for styrene 17-75 % (1991-1994), benzene and formaldehyde 0.5-0.7 % (1992, 1994)*.

Compared to the year 1991, the pollutant concentrations in the air of Kohtla-Järve have decreased, which is in some cases directly dependent on the amounts of pollutants emitted into air (Fig. 5), and the quantity of processing of raw materials, etc. If in 1990-1992 more than 50 % of phenols on Kohtla-Järve area (about 46-51 t all together) were coming from the mineral wool factory, then during the next years the phenols from oil shale processing installations prevailed (80-90 %). The mean and maximum concentrations at 95 % probability for benzene and toluene (Table 3) are directly dependent on amount of pyrolysis oil (imported raw material) which processing in period of 1991-1993 was decreased by 65 %.

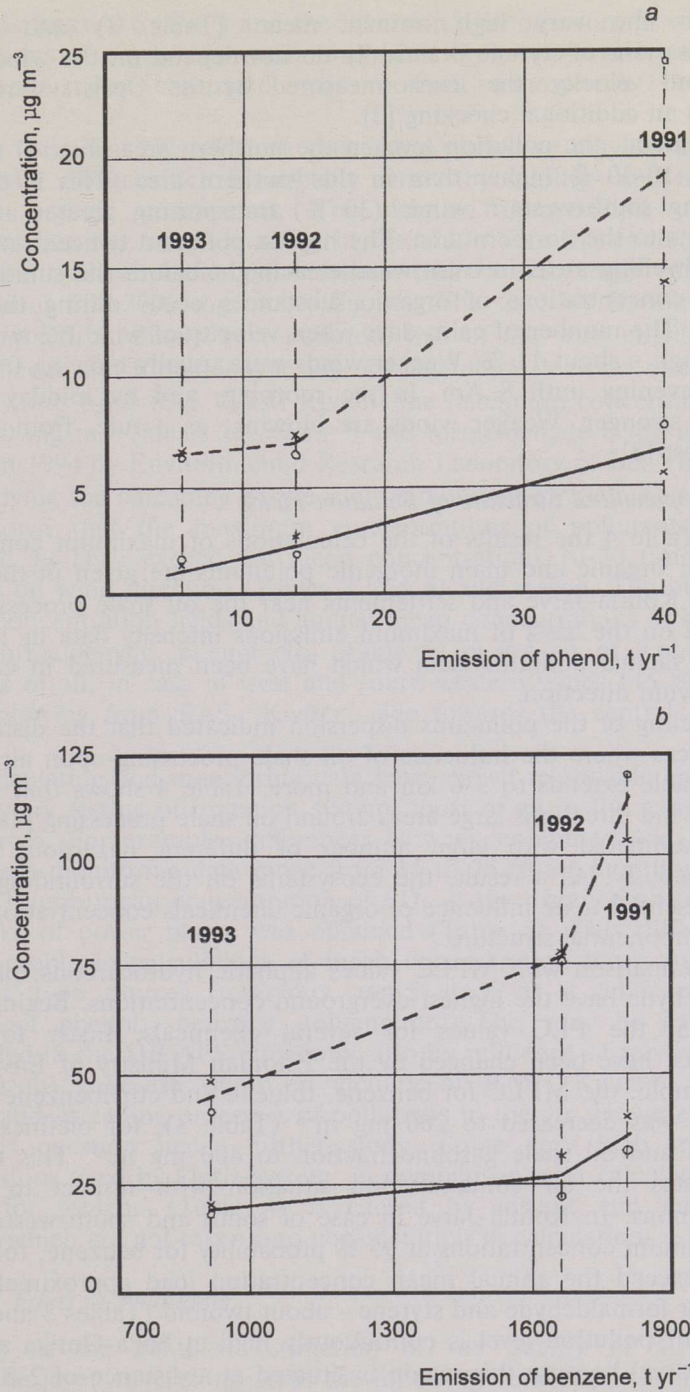* Those data with respect to MPLC values until 01.01.95 are given.

Fig. 5. Dependence of phenol and benzene concentrations in the air of Kohtla-Järve on emission quantity of pollutants: "━━━━━━" - annual mean; "━━ ━━ ━━" - maximums at 95 % probability; " o " - by south-west winds; " * "- by west winds

Since the very high annual mean (Table 3) and maximum concentrations of styrene practically do not depend on the wind direction and wind velocity, the levels measured by the Opsis-system have to undergo an additional checking [3].

In general, the pollution level in the northern area (Fig. 4) of Kohtla-Järve is 10-30 % higher than in the southern area. This is due to the prevailing south-western winds (30 %) transporting greater amounts of pollutants to the northern area. The highest pollutant concentrations occur in the dwelling areas in calm weather at night before the sunrise and the highest concentrations of organic substances occur during the summer months. The number of calm days when velocity of wind below 2 m s^{-1} is rather high - about 11 %. Weaker winds were usually blowing from 8 p.m. in the evening until 8 Am. in the morning, and by midday the wind became stronger. Weaker winds are blowing, as a rule, from south and south-east [3].

Multicomponential Structure of Pollution Fields

In the Table 4 the results of the calculations of maximum concentration levels for organic and main inorganic pollutants are given in the dwelling areas of Kohtla-Järve and settlements near the oil shale processing plant, obtained on the basis of maximum emissions intensity data in 1991-1994, and the factual pollution data which have been measured in case of the critical wind direction.

Modeling of the pollutants dispersion indicated that the distance from the sources where the influence of oil shale processing upon air quality is considerable extends to 3-6 km and more. Table 4 shows that in case of critical wind directions large areas around oil shale processing plants would be contaminated with large number of different hazardous chemicals simultaneously. As a result, the ecosystems on the surrounding areas lie under essential toxic influence of organic chemicals concentration fields of multicomponential structure.

In comparison with MPLC values aliphatic hydrocarbons, phenol and formaldehyde have the highest overground concentrations. Beginning from 1.01.1995, the PLC values for several chemicals, firstly for organic pollutants, have been changed by the Estonian Ministry of Environment. For example, the MPLC for benzene, toluene and ethylbenzene and their mixtures was decreased to 200 mg m^{-3} (Table 3), for olefines (hexene, heptene) and oil shale gasoline fraction to 400 mg m^{-3}. This essentially complicates the air contamination situation with respect to aromatic hydrocarbons. In Kohtla-Järve in case of south and south-western winds the maximum concentrations at 95 % probability for benzene, toluene and phenol exceed the annual mean concentration load approximately 4.5-9 times, for formaldehyde and styrene - about twofold (Tables 3 and 4).

The air pollution level is continuously high at Saka-Ontika area (near Kohtla-Järve) because this region is situated at a distance of 2-3 km from the oil shale processing and mineral fertilizer plants, on the leeward direction of the south (15 %) and south-west (up to 30 %) winds. The coincidence of calculated and measured data is satisfactory. A more hazardous situation in this region occurs under the conditions of very light

south winds (max. 0.6 m s^{-1}) and the inversion phenomenon, at which the concentrations of organic contaminants (also H_2S, NO_2, NH_3, etc.) rise twofold and more compared with normal atmospheric conditions (Table 4).

Besides this, near the oil shale processing plants we may always smell an unpleasant odour which is probably caused by sulphur- and nitrogen-containing organic compounds. The detailed composition of those components has not been identified in the air to far. The contamination level of air with aliphatic hydrocarbons may be very high (maximum concentrations 800-3000 mg m^{-3} - Fig. 4). The town of Kiviõli and its surroundings (Erra, Püssi) were polluted, first of all, with ethylbenzene, styrene, phenol and formaldehyde [9]. At Uuemõisa (leeward direction of the south winds from RAS "Eesti Kiviõli) the maximum concentrations of phenol 110 mg m^{-3} (mean 23 mg m^{-3}) and formaldehyde 8 mg m^{-3} were recorded in 1994 by Environmental Research Laboratory of Ida-Virumaa.

By studying the spreading of the multicomponent air pollution influxes it was shown that the maximum concentrations of pollutants in the overground air layer exceed the mean concentrations 10-30 times, more depending on wind direction (Tables 3 and 4) and season. The maximum values of concentration fields and annual mean concentrations of benzene, toluene, formaldehyde, phenol etc. (Table 5) in the air of Kohtla-Järve occur, first of all, in case of west and south-western winds (45 %), when they are blowing from RAS "Kiviter" side towards the central dwelling area.

The calculating and monitoring data have shown reasonable agreement by preliminary testing of imitation system, most of all in the case of high point sources. For example, differences between computed and fixed by Opsis-system monitoring data range from 15 to 25 % for monthly, annual and wind rhumb mean concentration of SO_2 at the distance up to 50 km from stacks of power plants was obtained (Table 5). This difference is more noticeable in calculations of mean concentration levels in case of lower area type sources (reservoirs, tanks etc.), as it takes place for emissions of phenols, benzene, toluene etc. This may be caused by nonrecorded in the DB APS emissions, also by influence of relatively high (over 100 m) coke-ash dump in vicinity of RAS "Kiviter" to wind direction and spreading processes of pollutants in the air. However, in the future this question needs further study. Some very high maximum concentrations fixed by Opsis-system, in comparison with calculations, for example for toluene (Table 4) is caused by instant and emergency emissions which are not taken into consideration in calculations.

Synergetic Effect of Pollutants

According to the complex estimation of the quality of air of the atmospheric layer at dwelling areas the following conditions for pollutants having synergetic effect should be accomplished [1]:

$$K = C_1/MPLC_1 + C_2/MPLC_2 + \ldots + C_n/MPLC_n < 1 \qquad (5)$$

Here C is the maximum concentration of individual components on the observed area.

Table 5. **The Wind Rhumbs Mean Concentrations ($C_{kr,j}$) of Pollutants by Monitoring (1) and Calculated (2) Data in the Centre of Kohtla-Järve (in Point C with Coordinates X = 46000 m and Y = 73000 m - Fig. 5), μg m⁻³ (1992-1993)**

Wind rhumbs	Benzene		Toluene		Phenol		Sulphur dioxide (1993)		
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	Wind direction from TPP
N	12.5	19.2	14.3	8.2	1.3	0.2	3	3	
NO	12	19.2	12	8.5	1.4	0.2	6	4	
O	10.8	19.2	14.3	8.5	1.6	0.2	10	12	Baltic & Estonian TPP
SO	12.1	19.2	19.8	8.5	2	0.2	11	9	Ahtme TPP
S	11.8	19.2	13	8.5	1.7	0.3	9	6	
SW	27.9	110.2	29.8	47.5	4.7	1.2	44	63	RAS Kiviter
W	33.8	23.8	66.9	17.6	3,8	0.3	20	17	Kohtla-Järve TPP
NW	14.7	19.2	30.7	9	2.1	0.2	3	4	
Annual mean	19	46.7	23	20.5	7	8.5	12-15	14	

Table 6. **The Synergetic Effect of Pollutants on the Saka Area by South and South-Western Winds (March-May, 1994)**

Pollutant	MPLC, mg m⁻³	Concentrations, mg m⁻³						
		1	2	3	4	5	6	7
Formaldehyde	35	8	15	7	12	24	10	27
Ammonia	200	90	110	70	50	290	90	110
Hydrogen sulphide	8	2	5	18	4	5	12	8
K		0.93	1.6	2.8	1.22	2.76	2.33	2.32

On the surroundings of the oil shale plants there is actual formation of the following synergetic groups where the organic components are present :

- formaldehyde + ammonia + hydrogen sulphide;
- formaldehyde + hexane + nitrogen dioxide + carbon monoxide;
- hexene + sulphur dioxide + nitrogen dioxide + carbon monoxide;
- formaldehyde + ozone(photo-oxidant) + nitrogen dioxide;
- formaldehyde + phenol + acetone + furfurole;
- phenol + sulphur dioxide + nitrogen dioxide + carbon monoxide.

This complicates the air pollution situation on the polycomponential fields still more. Presence of relatively high concentrations of organic components, such as formaldehyde, phenol, hexane and hexene increases the toxic level of atmosphere if the inorganic pollutants (SO_2, NO_2, CO, etc.) are continuously present. Such a situation is taking place frequently

(about 40 %) on the areas of Kohtla-Järve and Saka-Ontika by south and south-western winds (Table 4). In Table 6 the values K are taken for several real situations of Saka in spring of 1994. By S and SW wind directions the MPLC values are exceeded 1.2-2.76 times, whereas the share of formaldehyde in those levels is up to 33 %. Approximately the same situation takes place for the other groups where phenol and aliphatic hydrocarbons are present.

Thus, in the areas situated in the prevailingly leeward direction from RAS "Kiviter" continuously high air pollution levels may be recorded, which is caused by the simultaneous effect of organic and inorganic pollutants.

Summary

The basic principles of the imitation system for estimating and predicting of pollutants concentration fields in the overground air layer over the landscapes have been developed. The system makes it possible to calculate the mean and short-time maximum pollution level in an optionally given point or area depending on emission intensity, wind parameters and other conditions.

The results of calculations obtained on the basis of the imitation system and monitoring data show that, caused by a large number of sources and complicated chemical composition of discharges, the overground atmospheric air above the pollution fields of NE Estonia is characterized, as a rule, by multicomponential composition. Primarily, this is typical for dwelling and natural areas near oil shale processing plants, where the organic substances from industrial processes constitute 25-28 % of all pollutants. In the Regional Data Bank of NE Estonian Air Pollution Sources over 30 different organic substances have been detected.

Acknowledgments

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