OBSTACLES TO REHABILITATION OF DIOXIN POLLUTION "HOT POINTS" IN RUSSIA

Amirova Z*

Environmental Research&Protection Center, 450075, 147, October Avenue, Ufa, Russia

Introduction

Ratification of the Stockholm Convention by the Russian Federation in 2011 has not yet sufficiently prompted the activity in the field of cleanup of POPs polluted areas. In 2010 a project of the National Plan for realization of terms of the Stockholm Convention in the Russian Federation was presented. The source information for it was analysis of available separate data on studies in the field of POPs and the experience of the estimated dioxin inventory carried out in Russia in 2007. It was calculated that dioxin emission into the air from different sources in Russia makes 1784.4 g TEQ PCDD/Fs. The largest contribution into the total dioxin emission is made by burning solid waste landfill sites (35.3%), ferrous and non-ferrous metallurgy (28.3%) and building material industry (13.6%). The share of chemical industry is assessed as 0.02% (!), and burning of hazardous waste – 6.72%[1]. With total lack of monitoring dioxin emission produced by waste burning plants, power plants, hazardous waste incinerators including those burning medical waste in Russia, these conclusions require at least more precise assessment.

Besides emission from stationary sources there are dioxin polluted areas with high dioxin concentration formed due to production of chlorophenol products, 2,4,5-T, 2,4-D and others. Most known dioxin polluted areas are in the regions of the Urals and Povolzhje, these are the plants of the net "Khimprom" in Ufa and Chapayevsk. Some of these plants have been shut down, in Chapayevsk – from 2000, in Ufa from 2004 after a bankruptcy procedure. Monitoring of polluted areas in Ufa has been carried out from 1996. Primary assessment of variants for rehabilitation of the industrial zone but not the urban territory was made on the basis of the obtained data. In Chapayevsk partial replacement of the ground polluted up to 86.5 pg/g was carried out in the residential area but the plant territory was not subject to rehabilitation.

Material and methods

In the territory of the Khimprom plant the dioxin content was determined in soil, sludge, slit of treatment facilities and building materials. Most dangerous buildings and storages were examined for PCDD/Fs content[2]. Extraction methods were used for sample preparation. The clean-up procedure was performed by classical methods: multi-layer SiO_2, Al_2O_3 and Carbopac-C/Celite columns. PCDD/Fs determination in polluted samples was performed in compliance with the EPA 8280 methods. The measuring systems HRGC/LRMS: TRIO-1000 (1500), Carlo Erba 8035, DB-5 MS, 60 m, the detection limit was 0.3 ppb for solid samples, and INCOS 50 (Finnigan MAT), Varian 3400, DB-5 MS, 30 m. For PCDD/Fs measuring in urban soil samples a high-resolution mass spectrometer (Autospec-Ultima, VG, UK) and a series of isotope-labeled standards (CIL Corp.) were used in compliance with the USEPA 1613 method.

Results and discussion

Such a long period of producing dioxin hazardous products resulted in pollution of the Khimprom plant territory. The pollution level of industrial buildings is 5-18 ppb, pollution of soil in the territory of the plant - 0.2-10 ppb, the content in sludge pits is 3-70 ppb[3]. The soil samples at the depth of several meters contain dioxin from 0.4 to 12 ppb including. The highest pollution was found in the samples taken near a chlororganic waste incinerator that had been a source of dioxin emission for a long time. Pollution of the area within the radius of 200 meters beyond the plant territory exceeds 0.2 ppb, while the background level of soil pollution in the city and recreation areas does not exceed 3-8 ppt.

Now these territories present by themselves gradually dilapidating buildings with dismounted and removed equipment, and it is unknown whether cleanup from dioxins was carried out or not. In Ufa this process has resulted in "liquidation" of the most polluted shops by their destruction and storing building breakage in a new place within the same area (fig. 1). So far as this process was going on without following the norms of protection against spreading of polluted particles with high dioxin content (1-15 ppb); the results were clearly traced by the level of snow cover pollution[4].

Fig. 1. Storing of building breakage of destroyed buildings, Ufa, Khimprom, 2013

In the Russian Federation projects on liquidation of accumulated environmental damage of the past years had been developed. These projects were included into the program "Environmental safety of Russia" the realization of which began in 2013. For the plant in Ufa a project of liquidation of the dioxin pollution "hot point" was developed. It is supposed that reclamation of the "Khimprom" territory will take over two billion roubles. The Ministry of natural resources of the Russian Federation obliged itself to include this plant into the program of 2014 in priority order. In Chapayevsk the work on development of a program for rehabilitation of the polluted territory also began. Rehabilitation of soil in the residential area (soil removal and burial) was carried out.

However the present state of affairs is complicated by unpreparedness of the legislative and regulatory basis in Russia for making management and technical decisions on clearance. There are no norms of maximum dioxin content in soil of residential areas (interim standards of dioxin in soil make 0.33 pg/g), there are no norms for dioxin content in the air of the working zone, permissible emissions from incineration furnaces are not regulated (in some studies EU norms of 0.1 ng/m^3 are used).

But the main problem is the absence of the notion "the limit of clearance" for soil, waste, sludge and building materials polluted by dioxins. Calculation of hazard of sludge as waste carried out according to the criteria adopted in Russia refer the waste containing dioxin (and other POPs) over 1 ppb to IV or even to V class of hazard (practically to non-hazardous, at the level of domestic waste) because of low absolute concentrations.

Thus the Order of the Ministry of nature resources of the Russian Federation No. 511 "On setting of criteria for relating hazardous waste to a class of hazard for the environment" contains the method of assessment of waste hazard by calculation of the hazard factor K[5]. Five classes of hazard are singled out (Table 1).

Table 1. Classification of hazardous waste in Russia

Degree of hazardous impact of waste	Criteria of relating hazardous waste to a class of hazard for the environment	Class of hazard of waste for the environment	Degree of hazard of waste to the environment (K)
Very High	The environmental system is irreversibly deteriorated. There is no period of reclamation	Class 1 Extremely hazardous	$10^6 \leq K > 10^4$
High	The environmental system is strongly deteriorated. The reclamation period is no less than 30 years after the total liquidation of the source of hazardous impact	Class II Highly hazardous	$10^4 \leq K > 10^3$

Middle	The environmental system is deteriorated. The reclamation period is no less than 10 years after reducing hazardous impact of the existing source	Class III Moderately hazardous	$10^3 \leq K > 10^2$
Low	The environmental system is deteriorated. The period of self-recovery is no less than 3 years	Class IV Low-hazard	$10^2 \leq K > 10$
Very low	The environmental system practically is not deteriorated	Class V Non-hazardous	$K \leq 10$

The factor of the degree of waste hazard to the environment **K** is calculated by the following formula:
$\mathbf{K = K_1 + K_2 + ... + K_n}$, where
K – factor of the degree of waste hazard to the environment;
$\mathbf{K_1, K_2, ...K_n}$ – factors of the degree of hazard of separate components of waste to the environment.
The factor of the degree of hazard of a waste component to the environment $\mathbf{K_i}$ is calculated by the formula:
$\mathbf{K_i = C_i / W_i}$, where $\mathbf{C_i}$ – the concentration of the i-th component in the waste (mg/kg waste);
$\mathbf{W_i}$ – factor of the degree of hazard of the i-th component of the waste to the environment (mg/kg waste).
ome of the given values of factors of the degree of hazard (W_i) including "dioxins" are given in Table 2.
Thus for "dioxins" this value makes 24.6 mg/kg, there are also "furans" for which this value is considerably higher - 359 mg/kg. Application of this method to the waste containing dioxins at the level of 1 ppb TEQ PCDD/Fs (1000 ng/kg) results in the value $K_{PCDD/F} = 4*10^{-6}$ and actually cannot influence the total value taking into consideration other components of the dioxin-containing waste (for example, wall plaster).

Table 2 Factors of the degree of hazard (Supplement to the Order No. 511)

Name of component	W_i , mg/kg	Name of component	W_i , mg/kg
Aldrin	138	Lindane	4634
Benz(a)pyrene	59.97	Pentachlorbiphenyls	59.98
Hexachlorbenzene	354	Pentachlorphenol	75.85
Dioxins	24.6	Trichlorbenzene	598.4
Dichlorphenol	39.8	Phenol	215.44
Dichlordiphenyltrichlorethane	213.8	Furans	359

There are still more question to the methods. Thus it is unclear whether TEQ value is used in calculations or concentrations of congeners PCDD and PCDF. So to be related to the 1st class of hazard a dioxin-containing waste should contain 250 g TEQ PCDD/Fs in 1 kg of waste. With evident unacceptability it was namely this method that was used to assess the hazard of building waste from destroyed shops and waste in sludge tanks.
Besides the calculation method, the Order No. 511 gives an experimental method of assessment based on biological testing. Reaction of daphnia and/or water plants on water extract of waste sample is used. The method is a priori unsuitable for PCDD/Fs due to their extremely low solubility.
The way out, to our opinion, is excluding POPs from the list of waste to which the effect of the document is applied as it was done with radioactive and medicine waste.

References
1. Project of the National plan for realization by the Russian Federation of the Stockholm Convention on persistent organic pollutants "GEF-UNEP-Russia" (2011); NGO "International project Center", Moscow: 1-240
2. Amirova Z, Kruglov E, Maystrenko V, Khizbullin F (2006) Organohal. Comp. 68: 2225-2228
3. Amirova Z, Kruglov E (2005) Organohal. Comp. 67: 2094-2098
4. Amirova Z, Khalilov R, Tagirova N (2012) http://www.dioxin20xx.org/pdfs/2012/1307.pdf
5. Order of the Ministry of nature resources of the Russian Federation No. 511 "On setting of criteria for relating hazardous waste to a class of hazard to the environment" (2011), Moscow