INFRASTRUKTURA I EKOLOGIA TERENÓW WIEJSKICH
INFRASTRUCTURE AND EKOLOGY OF RURAL AREAS

Nr 3/2007, POLSKA AKADEMIA NAUK, Oddział w Krakowie, s. 59–67
Komisja Technicznej Infrastruktury Wsi

Andrzej Czerniak, Agata Poszyler-Adamska

SOIL AND ASSIMILATORY ORGANS OF TREES AS INDICATORS IN DIOXIN MONITORING OF THE FOREST ENVIRONMENT

Summary

The balance of major processes of metabolism is the condition of a continuous existence of the forest ecosystem. Each significant change of chemical balance in the environment brings about disturbances to homeostasis, quantitative and qualitative succession of individual components of plant and animal world, resulting in degradation of forest environment. The initiation of the continuous complex forest areas monitoring dates back to the 80`s when a sudden increase of forests` stands segments dieback occurred. The network of forest monitoring is based on the fixed observation I and II spots (SPO). Monitoring research may be extended to other substances not included in the Polish Act if the spot pollution source imposes a serious burden on the environment. It corresponds mainly to the areas situated in the closest vicinity of industrial plants which may significantly deteriorate the condition of the environment. The plants in interest include: heat and power stations, combustion plants, aluminum works, chemical plants, cellulose works, iron foundries, and industrial and municipal refuse landfill sites.

The paper identifies main dangers posed to the forest environment resulting from emission and migration of polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) – compounds commonly called dioxins. Mechanisms of biological activity of dioxins are insufficiently investigated. A sequence of unfavourable changes in organisms as a result of exposition to dioxins has been observed. Dioxins reach human and animal organisms together with food, as well as while inhaling and penetrating through skin. Dioxins damage living cells and as a consequence cause growth and development disorders of organisms. A symptom of dioxin intoxication in humans is *chloracne (acne chlorica)*, characterized by disorders in both anatomy and activity of sebaceous glands. The acne symptoms are only signs which indicate a general intoxication with chlorinated hydrocarbons.

The paper presents representative results of the investigation obtained within the confines of the introductory dioxin monitoring carried out in the selected forest complexes. Table 1 presents the results of the analysis of forest soil from unpolluted areas (the Antonin Forest Division - Czarnylas Forestry and the Gniezno Division - Orchówek Forestry) and a comparison with the results of polluted soil measurement collected in the vicinity of Warsaw where the earlier-conducted investigations showed the general dioxin content at the level of 12.275 ng PCDD/F-TEQ/kg of soil.

The carried out research proves that dioxins may accumulate both in soil and plants, and include them in food system. To maintain the chemical balance in forest areas the authors suggest covering a selected group of forest biotopes situated in the vicinity of major emitters of chemical pollution for dioxin monitoring.

Key words: dioxins, monitoring, forest, contamination

INTRODUCTION

Spreading of pollution in the environment is controlled in Poland by the System of State Monitoring of the Environment. It was constructed on base of the Environmental Protection Inspection Act dated July 20, 1991. Environmental monitoring is a system of observations and measurements of one or more natural components aiming at defining the state of the environment and changes taking place, as well as predicting future conditions. The idea of monitoring consists of conducting observations and measurements applying standardized apparatus, homogenous method, continuously, in numerous places and at the same time. The aims of monitoring are: atmospheric air, noise and radiation, surface and underground waters, as well as the Baltic Sea, soil surface, refuse and segments of animated nature and forest monitoring.

The necessity of defining the forest damage level in Poland results from a strong impact of chemical pollutions generated by industry. The initiation of the continuous complex forest areas monitoring dates back to the 80`s when a sudden increase of forests` stands segments dieback occurred. The network of forest monitoring is based on the fixed observation I and II spots (SPO).

Forest monitoring is a system of forest environment evaluation and sanitary condition on the basis of continuous or periodical observations and measurements of the selected indicators in the observation spots. The most vital goals and tasks of forest monitoring are: defining spatial diversity of forest sanitary state, observing changes in forest sanitary state taking place in time, analysis of cause - effect dependences between forest sanitary state and biotic and abiotic environmental factors, as well as working out short-period forecasts of forest sanitary state changes. An additional duty is to fulfill the obligations undertaken by Poland concerning the frame of the Transborder Long Distance Migration of Pollution Convention, Biodiversity Convention, as well as the Strasburg resolution and Helsinki Paneuropean Conference of Ministers called to discuss Forest

Protection in Europe, and EU Regulation No 2152/2003 (Forest Focus). The process of changes and adjustments of the monitoring to the EU demands began in 2004. The state forest monitoring programme introduced then the principle of two-level differentiating of the density of the networks of the Fixed Observation Spots: local and European. Forest monitoring includes tree stands damage monitoring, soils, health state of pine seeds, entomological, phytopathological, pollution deposits, monitoring of under-canopy precipitation and soil solutions. Within the frame of pollution deposits monitoring, the concentrations of SO_2 and NO_2 are measured and chemical composition of atmospheric precipitations is described. Chemical analyses comprise the measurements of chemical elements and compounds: Ca, K, Mg, Na, NH_4, Cl, NO_3, SO_4, Al, Mn, and Fe, as well as the trace elements.

Monitoring research may be extended to other substances not included in the Polish Act if the spot pollution source imposes a serious burden on the environment. It corresponds mainly to the areas situated in the closest vicinity of industrial plants which may significantly deteriorate the condition of the environment. The plants in interest include: heat and power stations, combustion plants, aluminium works, chemical plants, cellulose works, iron foundries, and industrial and municipal refuse landfill sites.

It is possible to detect and mark the compounds which occur at low concentration levels in environment, such as dioxins. Dioxins (PCDD/PCDF) are a group of compounds which includes organic compounds having a similar structure, containing chlorine and having similar physico-chemical properties, as well as the same or similar toxicity mechanism to 2,3,7,8-TCDD (the most toxic dibenzodioxin) [7]. The necessity of controlling dioxins dispersion results basically from both their negative impact and still not completely described mechanism of their influence on living organisms. The most significant sources of dioxins production are: combustion processes (including forest fires), the activity of factories and industrial plants such as heat and power plants, chemical plants, iron and color metals foundries, and road transport (mainly public). The important source of dioxins production is uncontrolled processes of organic compounds combustion which include chlorine-containing chemical substances. Local dioxin contaminations may rise during fires of dumping sites as well as explosions of transformers.

Mechanisms of biological activity of dioxins are insufficiently investigated. A sequence of unfavourable changes in organisms as a result of exposition to dioxins has been observed. Dioxins reach human and animal organisms together with food, as well as while inhaling and penetrating through skin. Dioxins damage living cells and as a consequence cause growth and development disorders of organisms. A symptom of dioxin intoxication in humans is *chloracne (acne chlorica*), characterized by disorders in both anatomy and activity of sebaceous glands. The acne symptoms are only signs which indicate a general intoxication with chlorinated hydrocarbons. The effects of dioxins toxicity influence comprise hyperplasia, as well as hyperkeratosis of epidermis between hair folliculi, hyperkeratosis of hair folliculi, as well as scaly metaplasia of sebaceous glands.

The balance of major processes of metabolism is the condition of a continuous existence of the forest ecosystem. Each significant change of chemical balance in the environment brings about disturbances to homeostasis, quantitative and qualitative succession of individual components of plant and animal world, resulting in degradation of forest environment. A chemical evaluation of the natural environment quality can also be conducted by applying an analysis of the following indicators: soil, water, air and bioindicators having a narrow range of tolerance in relation to a specific environmental factor.

The aim of the paper is to present the ways of dislocation and accumulation of dioxins in individual elements of the forest environment and describing the potential need and range of dioxin monitoring conducted in forest areas.

Additional aim is to evaluate which element of natural environment (soil, assimilatory organs) will be the best indicator of contaminated forests by dioxins.

METHODS OF RESEARCH

The paper presents representative results of the investigations obtained within the confines of the introductory dioxin monitoring carried out in the selected forest complexes. Table 1 presents the results of the analysis of forest soil from unpolluted areas (the Antonin Forest Division-Czarnylas Forestry and the Gniezno Division-Orchówek Forestry) and a comparison with the results of polluted soil measurement collected in the vicinity of Warsaw where the earlier-conducted investigations showed the general dioxin content at the level of 12.275 ng PCDD/F-TEQ/kg of soil [3]. *Pinus sylvestris* L. and *Betula pendula* Roth were also considered in dioxin monitoring as arborescent bioindicators commonly used in forestry. The dioxin content in the analysed assimilatory organs of both species was compared with the investigation carried out for needles and leaves collected from the areas possibly polluted with dioxins, i.e. from the post-fire areas from the Antonin Forestry Division. The pine tree stand fire took place in the third decade of April 2005; the samples were collected in the first decade of November 2005.

210 dioxins were identified and 17 most toxic congeners were determined to evaluate the potential toxicity of the samples. The level total of sample toxicity was defined as TEQ (Toxic Equivalency) which was calculated from the result of PCDD/PCDF (Toxic Equivalency). Toxic Equivalency was calculated from the result of analyses for mass concentration of all congeners of PCDD and PCDF in which 2,3,7,8 positions in the molecule are substituted by chlorine

atoms. The numerical value of TEQ is a total of partial parameters obtained by multiplication of an analytical result of mass concentration of an individual congener by respective TEF value. The result was given in standard units nanograms per kilogram of the analyzed material. The results of the analyses presented in the paper were carried out by the gas chromatography technique linked with mass spectometry with a double fragmentation of the investigated molecule utilizing devices of MAT GCQ and GC-MS/MS type. The research was carried out together with the certified Laboratory of Section of Trace Analyses of the Institute of Chemistry and Non-Organic Technology of the Cracow University of Technology.

3. RESULTS

Dioxins in soil

Atmospheric precipitation, solid and liquid waste disposal, ashes and dusts can be the source of dioxins in soil. The level of dioxin concentrations in soil varies and depends on a variety of factors: the depth of the investigated horizon, the adsorption force of PCDD/PCDF on soil molecules, the type of soil, soil-moisture and the degree of percolation, as well as soil reaction. The vertical movement of dioxins depends on the degree of saturation of sorption spots, migration of organic solvents or mixing of soil horizons. Dioxins accumulate mainly in the horizon 15-30 cm, in sandy soil they may migrate down to 100 cm. From the point of view of the threat to living organisms, the mobility of dioxins in soil, as well as their movement down to water-bearing horizons are crucial. The investigations proved a moderate susceptibility of dioxins to eluviation by precipitation water [4]. There is a certain threat of relocation of dioxins as a result of surface soil horizons erosion. Rappe`s investigations [8] show that the concentration of PCCD/PCDF in soil depends also on the ways of its utilization. In case of agriculturally utilized soils, where mixing of horizons takes place during conducted practices dioxins are washed out or dislocated to deeper soil horizons. The level of dioxin content in grasslands situated in the vicinity of the emitter did not exceed the value of 2.3 ng TEQ/kg, and in arable lands - 1.7 ng TEQ/kg. The dioxin level in forest soils in forest habitat reached the value of 38.0 ng TEQ/kg, and in coniferous forests habitats - 36.9 ng TEQ/kg.

The investigations carried out in ecologically pure areas (e.g. The Tatrzański and Magurski National Parks) showed the concentration of dioxins at the level of 1.0-5.0 ng-TEQ/kg, while the soil research conducted by the authors in the two forest divisions (Antonin and Gniezno) not neighbouring directly with pollution emitters proved low contents of dioxins in soil samples. The determined values occurred within the range from 0.4832 to 0.7210 ng PCDD/F-TEQ/kg and did not exceed the value of 4.706 ng PCDD/F-TEQ/kg of soil (Table 1). Thus the level of 5.0 ng-TEQ/kg should be considered as the level of the natural background of the chemical processes taking place in the environment [2]. The value can be useful to compare procedures purposes applied while investigating the soil environment.

The research carried out in 1997-2000 by Grochowalski in industrial areas [3] showed the presence of concentration of dioxins in the surface soil horizon at the level of 10.0-20.0 ng-TEQ×kg^{-1}. In the areas where household refuse is combusted (in Cracow) the content of dioxins in the surface soil horizon reached the value of 850.0 ng-TEQ×kg^{-1}.

Dioxins in water and bottom sediments

It can be generally seen that dioxins are poorly soluble in water which is directly connected with their structure and physico-chemical properties [3]. Dioxins reach waters mainly in the places where municipal and industrial sewage is disposed of, as well as a result of washing out of pollution from soil. Dioxins adsorb themselves on the surface of molecules of substances suspended in water, and next fall to the bottom. That is why the investigation concerning the degree of water pollution should be concentrated mainly on defining the concentration of dioxins in bottom sediments. According to the carried out investigation, over 90% of 2, 3, 7, 8-TCDD can be absorbed in water either by suspended molecules or bottom sediments [6]. The research showed also trace amount of dioxins in samples of sedimentary deposits dating back to the period before 6000 B.C., collected in Japan [5]. Prior to the intensive industrial development, the composition and ratio of the individual congeners in the analyzed samples was significantly different, comparing to the present analyses. This proves a clearly anthropogenic origin of those compounds in the environment. On the basis of the analyses of bottom sediments it can be observed that an abrupt dioxin increase began in the 30`s and reached its peak in the 70`s. A decrease of the content of those xenobiotics has been recorded since the beginning of the 80`s of XX century. It results, among other factors, from lower production of herbicides based on derivatives of chlorophenoxyacetic acids and polychlorinated biphenyls and from result of applying improved and cleaner production technologies.

Dioxin monitoring should basically cover the forest areas directly adjacent to chemically polluted watercourses and reservoirs as well as surfaces fertilized with liquid wastes.

Dioxin monitoring in plant and animal organisms

Dioxin monitoring first of all includes the consumption plants [3]. The plants cultivated in the open air in the areas industrially polluted and expose of a permanent dust fall from the air, contain toxins between 0.6-11.0 ng-TEQ/kg count out in dry mass. In the areas where meadows are burnt and household refuse is combusted in home stoves, the content of dioxins in leafy plants may reach 11.0 ng-TEQ/kg. Investigation of the assimilatory organs of aborescent bioindicators carried out in polluted areas showed a high accumulation of dioxins in the leaves of *Betula pendula Roth* (126.960 ng-TEQ/kg). In the samples collected from the control areas, the concentration was many times lower (1.2089 ng-TEQ/kg). The content of dioxins in the needles of the *Pinus silvestris* L. growing in polluted areas was 25.335 ng-TEQ/kg. In pine needles collected from the control areas the dioxin content reached the level of 0.618 ng-TEQ/kg (Table 1).

The investigation proved a high assimilability of dioxins by *Betula Pendula* Roth. This species, just as in case of the trace elements, can be a bioindicator in the dioxin monitoring of the forest environment.

The dioxins contained in the plant tissues enter food chains and are strongly accumulated in animal lipid tissues. Relatively high concentrations of dioxins are observed mainly in beef fat and meat, and to lower extent in pork. The content of dioxins in animal tissues results from the type of the fodder used. The chemical mobility of 2, 3, 7, 8-TCDD (the most toxic dioxin) comes from the properties of the chlorine atoms, and that is why this dioxins is very slowly introduced into the cycle of metabolism conversion, or is decomposed within the period of tens of days. According to their hydrophobic properties, dioxins locate themselves in fat-rich tissues, and the capability of donor-acceptor reactions with various endogenous substances facilitates their penetration through various biological barriers of the living organism and placing themselves in liver, spleen, hypophysis and other organs. 2, 3, 7, 8-TCDD can be called a total poison from bacteria to humans.

Investigations focusing on the description of dioxin content in wild animals' meat utilized for consumption purposes have not been carried out in Poland so far. Pilot studies should include populations of big game deer (roe deer, stags and fallow deer), as well as wild boars living in heavily polluted areas.

Dioxin's decomposition and their migration

It is assumed that decomposition half-period of dioxins in the environment under the influence of various factors may last for a few years. For instance the degradation of 2, 3, 7, 8-TCDD in soil at the depth of 15 cm takes place after 14 years. Some microorganisms show the capability of dioxin decomposition without any side effects for themselves. *Phanerochaete chrysosporium* (capable of decomposing also DDT) and soil bacteria *Pseudomonas* and *Arthrobacter* may serve as an example. Biodegradation is a very slow process, depending on many factors such as: reaction, moisture, temperature and the presence of metals which catalyze the processes. Ultra-violet radiation significantly influences the reduction of the amount of dioxins in the environment. The sequence of investigations carried out in laboratories in the US, Italy and Poland [3] proved that photolithic degradation takes the highest pace on tree and grass leaves. The consequence of the photolithic degradation is new products with a lower number of chlorine atoms, and thus lower toxicity.

Xenobiotics of PCDD/PCDF - type introduced into the environment as a result of human activity and coming into existence in a natural way owing to the processes occurring in the environment are subject to general dynamics laws of substance dispersion both in the atmosphere, lithosphere, hydrosphere and biosphere. Compounds emitted into the atmosphere, adsorbed on dusts and smokes, can move to long distances and significant heights under favourable meteo and topographic conditions. Thus migration of dioxins can be both vertical and horizontal. It usually causes pollution of soils, water-bearing layers and, consequently, rivers and water reservoir. The result of the processes is further dispersion of dioxins in biosphere, and nutrients intake by root systems, and further – contamination of both carnivorous and herbivorous organisms.

Forecasting of the possible ways of dioxins dispersion in the environment is an extremely difficult task due to large number of media in which they occur, as well as possible chemical, biological and metabolic transformations they are subjected to. The evaluation of environmental contamination can be carried out by monitoring of proper environmental indicators and sources of dioxin emissions which are mainly smokes and dusts disposed to the environment by industrial and power station chimneys, ashes, sediments and post-industrial sludge investigation. Biological monitoring is connected with dioxin transformation in living organisms, toxicological – corresponds to the investigations on post-disease effects of a given human population, and chemical – the methods of detecting, identification and dioxin determination in environmental components.

CONCLUSIONS

Migrating and accumulating dioxins may pose a direct danger to some forest ecosystems. Selected forest biotopes and biocenosis situated in the vicinity of major chemical pollution emitters should be included in the dioxin monitoring to keep the chemical balance. The network of measurement-control spots, as well as the frequency of sample collection for chemical analyses from selected indicators should be agreed upon while preparing the principles of dioxin monitoring of selected forest complexes.

The research proved that *Betula pendula* Roth. for the sake of its huge cumulative properties can be qualified as a bionidicaror in the dioxin monitoring of forest monitoring. *Pinus sylvestris* L. proves also cumulative properties but in a lower extent. That is because wax substances covering trees, shrubs and grass leaves are active donors of hydrogen atoms which activate themselves towards the xenobiotics in the presence of ultraviolet light. Additional research should be carried on to find other bioindicators in the dioxin monitoring.

In the examined forestries, dioxins did not accumulate in soil and water. It means that the examinated areas were comparatively non-polluted. Soil reached by substances providing hydrogen, owing to its physical condition, structure and presence of lipid-philic compounds, brings about dissolution of dioxins in the first stage, and, afterwards, their transportation to deeper layers, where the process of photolithic degradation is obstructed to a high degree. Low content of dioxins in soil may imply that dust contamination can be taken by assimilatory organs of trees.

REFERENCES

[1]Beck H. et al.: *Occurrence of PCDD and PDF in different kinds of paper*. Chemosphere 1988.

[2]Czerniak A., Poszyler-Adamska A.: *Identyfikacja dioksyn w glebie leśnej- materiały konferencyjne* Międzynarodowej Konferencji Naukowej ENVIRO 2006 (w druku).

[3]Grochowalski A. *Badania nad oznaczaniem polichlorowanych dibenzodioksyn i dibenzofuranów i bifenyli*. Monografia 272, Kraków 2000.

[4]Helling, C.S., Isensee, A.R., Woolson, E.A., Enzor, P.D.J., Jones, G.E., Plimmer, J.R., & Kearney, P.C. *Chlorodioxins in pesticides, soils and plants.* J. environ. Qual., 2: 171-178, 1973

[5]Makles Z., Świątkowski A., Grybowska S.: *Niebezpieczne dioksyny.* Wyd. Arkady 2001.

[6]Matsmura F., Benezet H.J.: *Bioaccumulation and microbial degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin.* Environ. Health Perspect. 1973 s. 253-258.

[7]Płaza G.: *Dioksyny- niebezpieczne związki.* Ochrona powietrza i Problemy Odpadów.

[8]Rappe C., Kjeller L.O.: *PCDDs and PCDFs in environmental samples air, particulates, sediments and soil.* "Chemosphere" 1987 p. 1175-1780.

Andrzej Czerniak, Dr. Sc., Ph.D
Agata Poszyler-Adamska, M.Sc.
Department of Forest Engineering.
The August Cieszkowski Agricultural University
ul. Mazowiecka 41. 60-623 Poznań.
e-mail: aczerni@au.poznan.pl

Rewiever: *Prof. Czesław Rycąbel, Dr. Sc., Ph.D*