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EMISSION OF VOLATILE ORGANIC COMPOUNDS FROM FURNITURE SURFACES FINISHED WITH LACQUER COATINGS

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Abstract. The study presents results of the investigations on the influence of the presently produced furniture on the development of concentrations of volatile organic compounds and formaldehyde in air of rooms. The volatile organic compounds were analyzed with the use of the gas chromatography method together with mass spectrometry. The obtained results showed differences in type as well as in amounts of the identified compounds depending on the type of the applied materials for finishing furniture surfaces.

Key words: volatile organic compounds, formaldehyde, pollution of air in rooms, furniture, lacquers, environment protection

INTRODUCTION

The investigations performed in the number of laboratories in Poland and abroad [Berglund et al. 1997, Bluyssen et al. 1997, Berglund et al. 1999, Zabiegała et al. 2000] showed that air in rooms contains wide spectrum of different substances influencing hygienic conditions of rooms as well as human health. The source of emission of substances polluting air is located in rooms and consists of furnishings including furniture. Despite the fact that furniture is not the only source of harmful emission, it is subjected to special analytical control due to the publicized in last 10 years problems with emission of formaldehyde.

As long as the formaldehyde emission was until recently the essential parameter for the estimation of hygienic conditions, presently the important criterion of the estimation is defined as emission of volatile organic compounds (VOC).

The world health organisation has defined VOC as "organic compounds with boiling points between 50 and 260°C" [Barry and Corneau 1999, Henneuse-Boxus, Alevantis 1999], while the EU directive on dissolvents defines VOC as "chemical substances having at temperature of 293.15°K vapor pressure equal to or higher than 0.01 kPa" [Kershaw 1998].

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The main reasons of the VOC emission in furniture industry are lacquers which are commonly used for finishing furniture surfaces.

The level of the VOC emission depends not only on dissolvents and diluents but also on auxiliary substances, volatile monomers as well as low-molecular weight fractions in substances forming coatings and fractions emitted during curing processes of polycondensating binders [Proszyk 1999].

In many countries attempts are made to establish the maximum value of the acceptable level of emission of the total volatile organic compounds (TVOC). In Germany the Federal Environment Office proposed to award a quality mark for furniture for which the total emission of volatile organic compounds is lower than 300 μg m^{-3} [Salthammer and Marutzky 1995]. Wilhelm Klauditz Institut (WKI) in turn recommends on the basis of its own investigations to use recommendations limiting VOC emission to the level of 800 μg m^{-3} [Salthammer and Marutzky 1995]. While the Californian Department of Health Services certifies furniture quality when the emission of TVOC is lower than 500 μg m^{-3} and formaldehyde is lower than 0,05 ppm [Alevantis 1999]. In Poland the acceptable concentration of harmful substances in air of rooms of apartments and public buildings was presented in the directive of the Ministry of Health and Social Welfare from March 12, 1996. The directive contains a list of 35 substances for which the maximum level of concentration was defined.

The identification of the influence of the presently produced furniture on the development of concentration of volatile organic compounds in air of rooms is the essential condition for the improvement of hygienic conditions of rooms.

The objective of the investigations was to determine the level of hygienic conditions of the presently produced furniture. The scope of the investigations included determination of levels of emissions of volatile organic compounds and formaldehyde from furniture selected for the investigations.

MATERIALS AND METHODS

The research was performed for furniture produced in series by Polish factories and sold both at home as well as foreign markets.

The investigations were performed for a group of furniture made of oak wood and particle board veneered with natural oak veneer and finished with nitrocellulose stain, prime nitrocellulose lacquer and topcoat acrylic lacquer as well as made of MDF finished with prime and topcoat polyurethane enamels.

The investigations were made for samples of the following dimensions 50·100 cm. The samples were prepared in industrial conditions and two-sided coated with lacquers:

– sample A: particleboard veneered with natural oak veneer and finished with nitrocellulose stain with amount of 80 g/m^2, single layer of prime nitrocellulose lacquer with amount of 200 g/m^2 and single layer of acrylic lacquer with amount of 240 g/m^2,

– sample B: MDF finished with two layers of prime polyurethane enamel with amount of 2·200 g/m^2 and one layer of topcoat polyurethane enamel with amount of 170 g/m^2.

Determination of emission of volatile organic compounds

Volatile organic compounds were analyzed with the use of the gas chromatography method together with mass spectrometry.

The investigations were made in a chamber of volume of 1 m^3 in the standard conditions corresponding to the conditions of formaldehyde determination according to the recommendation RAL-UZ 38 [2002]. The following air parameters were used during the measurements: temperature ±23°C, relative humidity ±45%, ratio of air exchange 1 h^{-1} and chamber load 1 m^2/1 m^3.

Air was sampled after 24 hours starting from placing investigated elements in the chamber. For each sampling process two samples of air from the chamber were collected. Simultaneously ambient air sample was also taken. Volatile organic compounds were enriched with the adsorption method using solid sorbent consisting of sorption capillaries filled with synthetic sorbent Tenax of the amount of 80 mg. The capillaries before their use were heated in temperature of 250°C during 30 min. The amount of air flowing through the sorbent was ca. 5 liters. The analytes absorbed by the sorbent were thermally released in the desorber in temperature of 250°C. Time of desorption was 5 min. The released analytes were transported with inert gas of volume flow of 20 cm^3/min to a microcatcher. After finishing the desorption phase the analytes were thermally released form the microcatcher by heating in 250°C for 1 min. Next the analytes were directed to the front of the chromatographic column. The chromatographic analysis was performed for whole analytes desorbed in conditions presented in Table 1.

Table 1. Parameters of the analytical system TD/GC/MS
Tabela 1. Parametry układu analitycznego TD/GC/MS

Elements of the system Elementy układu	Parameters Parametry
Gas chromatograph Chromatograf gazowy	TRACE GC, Thermo Quest.
Column Kolumna	RTX – 624 Restek Corporation, 60m x 0,32mm ID D_f – 1,8 μm: 6% cyanopropylophenyl, 94% dimethylopolysiloxane RTX – 624 Restek Corporation, 60m x 0,32mm ID D_f – 1,8 μm: 6% cyjanopropylofenyl, 94% dimetylopolisiloksan
Detector Detektor	mass spectrometer (SCAN: 10 – 350) spektrometr mas (SCAN: 10 – 350)
Feeder Dozownik	thermal desorber connected with sorption catcher rinsing gas: argon 20 m^3min^{-1} rinsing time: 5 min termiczny desorber połączony z pułapką sorbcyjną gaz płuczący: argon 20 m^3min^{-1} czas płukania: 5 min
Microcatcher Mikropułapka	sorbent: 80 mg Tenax TA/30 mg Carbosieve III desorption temperature: 250°C during 60 s sorbent: 80 mg Tenax TA/30 mg Carbosieve III temperatura desorpcji: 250°C przez 60 s
Carrier gas Gaz nośny	helium: 100 kPa, ~2 cm^3min^{-1} hel: 100 kPa, ~2 cm^3min^{-1}
Temperature schedule Program temperaturowy	40°C during 2 min, 7°C min^{-1} to 200°C, 10°C min^{-1} to 230°C, 230°C during 20 min 40°C przez 2 min, 7°C min^{-1} do 200°C, 10°C min^{-1} do 230°C, 230°C przez 20 min

Compounds identification: The identification of the compounds was made on the basis of spectrum using the spectrum library NIST MS Search Program version 1.7. The identification was verified with the use of retention times of the compounds identified in the analyzed system.

Quantitative analysis: The quantitative analysis of the VOC emission was made by the use of the method of addition of the standard of 4-bromo-fluorbenzene, which was dosed by a capillary with sorbent in amount of 133 ng.

The VOC determination was made in two cycles, i.e. after 14 and 75 days after finishing elements with coatings.

Determination of formaldehyde emission

Measurements of formaldehyde emission were made with the use of the chamber method described in the standard PN-F-06106-2 (1994).

RESULTS AND THEIR DISCUSSION

The chromatographic analysis let to obtain chromatographic separation of volatile organic compounds emitted from the investigated surfaces. The chromatographs obtained in the first cycle of the investigations, i.e. after 14 days after finishing the surfaces with coatings, are presented in Figures 1 and 2.

During the first stage of the investigations the analysis of chromatographs and mass spectra was limited to the identification of peaks of high intensity. While in the second stage of the investigations the compounds were identified which were related to the main peaks in chromatographs obtained in the first stage of the investigations.

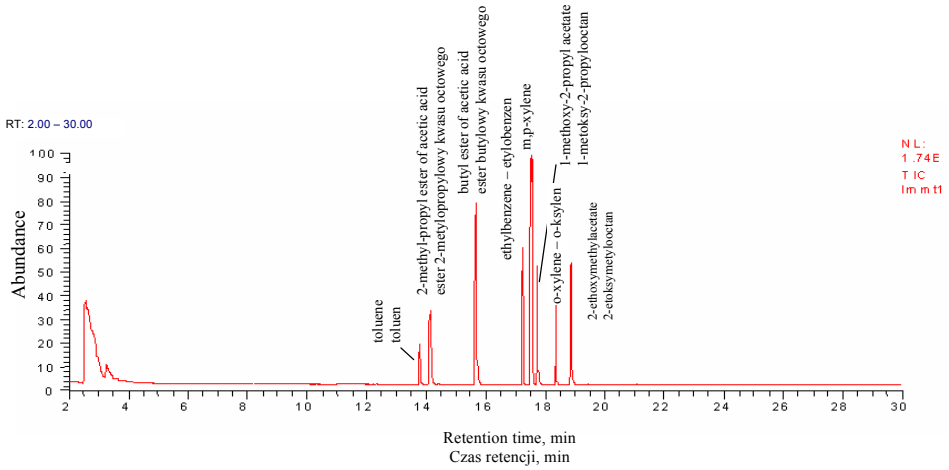


Fig. 1. Chromatograph of volatile compounds separation from samples of veneered particleboard finished with lacquer. The first stage of the investigations, sample A

Rys. 1. Chromatogram rozdziału lotnych związków z próbek płyty wiórowej fornirowanej lakierowanej uzyskany w pierwszym etapie badań, próbka A

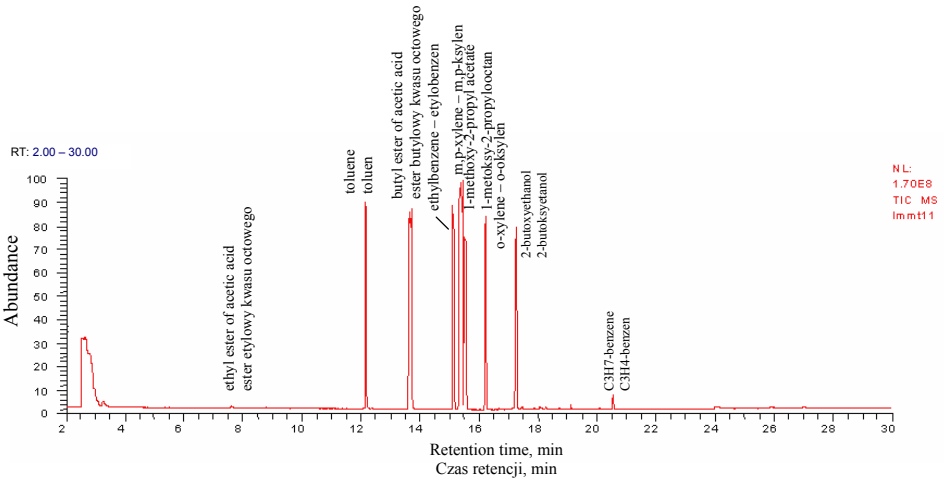


Fig. 2. Chromatograph of volatile compounds separation from samples of MDF finished with lacquer. The first stage of the investigations, sample B
Rys. 2. Chromatogram rozdziału związków lotnych z próbek płyty MDF lakierowanej uzyskany w pierwszym etapie badań, próbka B

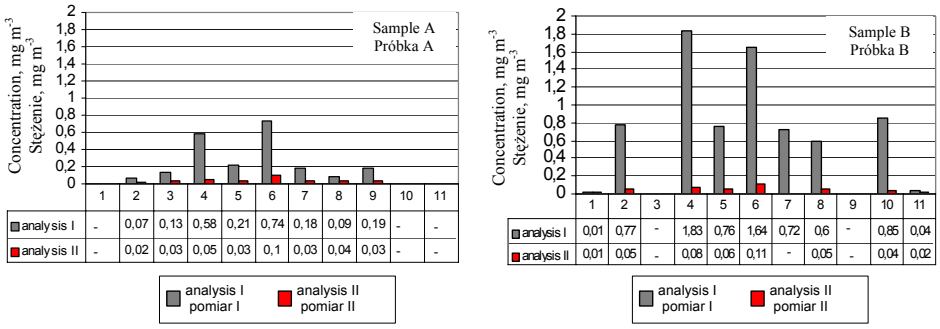
Amongst the isolated compounds there were mainly identified aromatic hydrocarbons, furthermore esters and alcohols. The dominating fraction of volatile compounds were aromatic hydrocarbons and their ratio to the rest of compounds was variable in individual tests.

In the case of veneered particleboard dyed with nitrocellulose stain and covered with prime nitrocellulose lacquer and topcoat acrylic lacquer (sample A) it was found that the subsequent peaks presented in chromatograph derive from toluene, 2-methyl-propyl ester of acetic acid, butyl ester of acetic acid, ethylbenzene, inseparated m,p-xylene, 1-methoxy-2-propyl acetate, o-xylene, 2-ethoxymethylacetate. On the other hand in the case of samples made of MDF coated with polyurethane enamels (chromatograph 2) the characteristic components of the emission were ethyl ester of acetic acid, toluene, butyl ester of acetic acid, ethylbenzene, inseparated m,p-xylene, 1-methoxy-2-propyl acetate, o-xylene and 2-butoxyethanol.

Figure 3 presents results of emission of volatile organic compounds from individual furniture coatings.

The analysis of the data presented in Figure 3 let to state that the dominating compound emitted from samples A was inseparated m,p-xylene. Its concentration in air sampled from the chamber in the first stage of the measurement cycle was equal to 0.74 $mg \cdot m^{-3}$. The concentrations of other identified compounds were as follows: butyl ester of acetic acid – 0.58 $mg \cdot m^{-3}$, ethylbenzene – 0.21 $mg \cdot m^{-3}$, 2-ethoxymethylacetate – 0.19 $mg \cdot m^{-3}$, 1-methoxy-2-propyl acetate – 0.18 $mg \cdot m^{-3}$, o-xylene – 0,09 $mg \cdot m^{-3}$ and toluene – 0.07 $mg \cdot m^{-3}$. In the case of samples B made of MDF coated with polyurethane enamels it was found in the first stage of the investigations that the very high emission of vapors of butyl ester of acetic acid (ca. 1.85 $mg \cdot m^{-3}$) as well as m,p-xylene (ca. 1,64 $mg \cdot m^{-3}$). The obtained values were much higher as compared to the elements made of particleboard finished with nitrocellulose and acrylic lacquers. The emissions of vapors of the identified

compounds were as follows: 2-butoxyethanol – 0.85 mg·m^{-3}, toluene – 0.77 mg·m^{-3}, ethylbenzene – 0.76 mg·m^{-3}, 1-methoxy-2-propyl acetate – 0.72 mg·m^{-3}, o-xylene – 0.60 mg·m^{-3}. However, the values reported for elements finished with polyurethane enamels are higher as compared to samples dyed with nitrocellulose stain and covered with prime nitrocellulose lacquer and topcoat acrylic lacquer.



1 – ethyl ester of acetic acid – ester etylowy kwasu octowego, **2** – toluene – toluen, **3** – 2-methyl-propyl ester of acetic acid – ester 2-metylopropylowy kwasu octowego, **4** – butyl ester of acetic acid – ester butylowy kwasu octowego, **5** – ethylbenzene – etylobenzen, **6** – m,p-xylene – m,p-ksylen, **7** – 1-methoxy-2-propyl acetate – 1-metoksy-2-propylooctan, **8** – o-xylene – o-ksylen, **9** – 2-ethoxymethylacetate – 2-etoksymetylooctan, **10** – 2-butoxyethanol – 2-butoksyetanol, **11** – trimethylbenzene sum – suma trimetylobenzenu

Fig. 3. Comparison of the results of emission of volatile organic compounds from samples A and B at two stages of measurements
Rys. 3. Porównanie wyników badań emisji lotnych związków organicznych z próbek A i B z dwóch etapów pomiarowych

The results of the performed chromatographic analysis also show that the concentration of the analyzed compounds was several times higher in the second stage of the investigations as compared to the first stage. The reduction of the emission of the analyzed compounds was varying form 50 to 100%. However, the reduction was higher for polyurethane enamels. While in the case of veneered particleboard finished with lacquers the concentration of the dominating compounds was reduced from 0.58 to 0.05 mg·m^{-3} for butyl ester of acetic acid and form 0.74 to 0.10 mg·m^{-3} for m,p-xylene, in the case of MDF finished with polyurethane enamels the concentration of vapors of butyl ester of acetic acid was reduced from 1.83 to 0.08 mg·m^{-3} and vapors of m,p-xylene reduced from 1.64 to 0.11 mg·m^{-3}.

The relative standard deviation values determined on the individual survey were within the range of 0.006-0.055 mg·m^{-3}, while the median relative standard deviation was within the range of 0.00-0.03 mg·m^{-3}.

In the first stage of the measurements the sum of concentrations of organic substances emitted from surfaces of particleboard finished with nitrocellulose stain, prime nitrocellulose lacquer and topcoat acrylic lacquer was equal to ca. 2190 µg·m^{-3}, while from MDF coated with polyurethane enamels it was 7220 µg·m^{-3}. As a result of seasoning the total emission was reduced from 2190 to 330 µg·m^{-3} and from 7220 to 420 µg·m^{-3} respectively.

The estimation of hygienic conditions of the investigated furniture was made with the use of the analysis of emission of volatile organic substances supplied by the determination of emission of formaldehyde. The investigated elements were characterized after 14 days of their production by low emission of formaldehyde varying from 0.038 $mg \cdot m^{-3}$ (furniture type A) to 0.043 $mg \cdot m^{-3}$ (furniture type B).

The comparison of the total values of the emissions of the tested elements to the international recommendations let to state that the investigated elements after 75 days for their production showed the emission which fulfills the requirements of WKI and the Californian Department of Health Service. However, the hygienic standards of the German Federal Environment Office (< 300 $\mu g \cdot m^{-3}$) were not fulfilled.

The obtained results as compared to the acceptable level of concentration of organic vapors and gasses contained in the directive of the Ministry of Health and Social Welfare from March 12, 1996 show that the concentrations of the individual identified compounds obtained the acceptable limits during the second stage of the investigations. The only exception was found for elements made of MDF and finished with polyurethane enamel. For the elements xylene vapors slightly exceeded the limit. It has to be emphasized that not all identified compounds were included in the mentioned directive of the Ministry of Health and Social Welfare from March 12, 1996.

FINAL REMARKS

The obtained results show that the investigated furniture may significantly influence concentrations of the volatile organic compounds in air of rooms during the initial period after the furniture production. Moreover, the results show that the found tendencies depend on the type of the applied wood finishes. The proper selection of the components of the finishes applied for furniture is the essential condition for fulfilling the current ecological standards.

In order to limit the emission of the volatile organic compounds from furniture surfaces it is necessary to approach reducing the content or even eliminating dissolvents from lacquers for wood finishing. The improvement of packing methods of furniture for instance by replacing air impermeable foils with perforated foils or by cardboard may contribute to reduction of the VOC emission from new furniture during the initial stage of their use when the highest emission of substances causing pollution of air in rooms was found. These potential solutions should be applied by furniture producers in order to fulfill the ecological standards as well as requirements of users.

CONCLUSIONS

1. The performed investigations showed that the presently produced furniture finished with conventional lacquers may cause temporary pollution of air in rooms.
2. The investigated elements showed the emission of formaldehyde not exceeding 0.05 $mg \cdot m^{-3}$, i.e. 0.04 ppm that is they fulfilled the international requirements.
3. The elements made of MDF finished with polyurethane enamels were characterized during the first stage of the use by higher level of emission as compared to elements made

of particleboard finished with nitrocellulose stain, prime nitrocellulose lacquer and topcoat acrylic lacquer.

4. There was observed distinct decrease of the VOC emission. After 60 days of seasoning it was found that the emission from the investigated elements decreased to the acceptable level values.

REFERENCES

Alevantis Leon E., 1999. Reducing occupant exposure to volatile organic compounds (VOCs) from office building construction materials: non- binding guidelines. Appendices. Environmental Health Laboratory Branch, Division of Environmental and Occupational Disease Control, California Department of Health Services.

Barry A.O., Corneau D., 1999. Volatile Organic Chemicals Emissions from OSB as a Function of Processing Parameters. Holzforschung 53(4), 441-446.

Berglund B., Clausen G., Ceaurriz J., Kettrup A., Lindvall T., Maroni M., Mřlhave L., Pickering A., Risse U., Rothweiller H., Seifert B., Younes M., 1997. Total Volatile Organic Compounds (TVOC) in Indoor Air Quality Investigations. ECA, Report No 19, EUR 17675 EN. Office for Official Publications of the European Community Luxembourg.

Berglund B., Bluyssen P., Clausen G., Garriga-Trillo A., Gunnarsen L., Knoeppel H., Lindvall T., MacLeod P., Molhave L., Winneke G., 1999. Sensory Evaluation of Indoor Air Quality. ECA, Report No 20, EUR 18676 EN. Office for Official Publications of the European Community Luxembourg.

Bluyssen P., Cochet C., Fischer M., Knoeppel H., Levy L., Lundgren B., Maroni M., Mřlhave L., Rothweiler H., Saarela K., Seifert B., 1997. Evaluation of VOC Emissions from Building Products (Soild Flooring Materials). ECA, Report No 18, EUR 17334 EN. Office for Official Publications of the European Community Luxembourg.

Henneuse-Boxus C.: Sampling and analysis of volatile organic compounds (VOC) emitted by materials. http://www.certech.be/ANG/index.htm

Kershaw I., 1998. Legislacja VOC na progu zmian. Część I. Farby lakiery 11, 16-20.

Proszyk S., 1999. Wybrane problemy z zakresu emisji lotnych składników organicznych z wyrobów lakierowych stosowanych w meblarstwie. In: Mater. Konf. Ergonomia i ochrona pracy w drzewnictwie oraz produkcji rolno-leśnej. 15-17 września 1999, Poznań-Kiekrz. Zastosowania Ergonomii 2/3 (34/35), 173-180.

PN-F-06106-2, 1994. Oznaczanie emisji formaldehydu metodą komorową.

Salthammer T., Marutzky R., 1995. Bewertungsverfahren für VOC –Emissionen aus Möbel aus deutsche und europäischer Sicht. In: Mater. Konf. Wymagania Unii Europejskiej a stan higieniczności mebli i materiałów stosowanych do ich produkcji. 4-5 grudzień 1995, Poznań--Kiekrz. ITD, 45-50.

RAL-UZ 38, 2002. Basic Criteria for Award of the Environmental Label. Low-Emission Wood Products and Wood-Base Products.

Zabiegała B., Przyk E., Przyjazny A., Namieśnik J., 2000. Evaluation of Indoor Quality on the Basis of Measurements of VOC Concentration. Chem. Anal. 45 (1), 11-26.

Zarządzenie Ministra Zdrowia i Opieki Społecznej z dnia 12 marca 1996 r. w sprawie dopuszczalnych stężeń i natężeń czynników szkodliwych dla zdrowia, wydzielanych przez materiały budowlane, urządzenia i elementy wyposażenia w pomieszczeniach przeznaczonych na pobyt ludzi. Mon. Pol. Nr 19, poz. 231.

EMISJA LOTNYCH ZWIĄZKÓW ORGANICZNYCH Z POWIERZCHNI WYROBÓW MEBLARSKICH USZLACHETNIONYCH POWŁOKAMI LAKIERNICZYMI

Streszczenie. Praca przedstawia wyniki badań wpływu obecnie produkowanych mebli na kształtowanie się stężeń lotnych związków organicznych i formaldehydu w powietrzu pomieszczeń. Lotne składniki organiczne analizowano techniką chromatografii gazowej w połączeniu ze spektrometrią mas. Uzyskane rezultaty wykazały różnice zarówno w rodzaju, jak i ilości identyfikowanych związków w zależności od rodzaju zastosowanych materiałów uszlachetniających powierzchnie wyrobów meblarskich.

Słowa kluczowe: lotne związki organiczne, formaldehyd, zanieczyszczenie powietrza wewnątrz pomieszczeń, wyroby lakiernicze, wyroby meblarskie, ochrona środowiska

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