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## ASSESSING THE MIGRATION OF ORGANIC HALOGEN COMPOUNDS FROM SEWAGE SLUDGE TO A LIQUID PHASE

As sewage sludge applied to arable land may contain organic contaminants such as PAHs, AOXs, and PCBs, it is necessary to investigate the penetrating power of these substances and the risk they pose to the environment. The study deals with the migration of organic halogen compounds from sewage sludge to a liquid phase, using *p*-chlorophenol as an example. It was found that the transition process was affected considerably by the *p*-chlorophenol concentration and low temperatures, especially due to freezing/thawing, because the binding of water with sludge was different.

### 1. INTRODUCTION

Under current state regulations [8], it is necessary to monitor the content of organic matter, biogenic substances and heavy metals if sewage sludge is to be applied to arable land. Although the requirements do not include the identification of such hazardous organics as PAHs (polycyclic aromatic hydrocarbons), AOXs (adsorbable organic halogens), PCBs (polychlorinated biphenyls) and PCDD/Fs (polychlorinated dibenzo-*p*-dioxins/dibenzofurans), their presence cannot be excluded [1]–[3], [5], [9]. These contaminants may pose considerable risk to human health and the environment because of their low biodegradability, high stability, toxicity and accumulation in soil. Nowadays, it is necessary to identify and assess not only the migration of heavy metals from the sewage sludge to the environment, especially to the liquid phase, but also the migration of organic halogens [4], [6], [11]. The problem is particularly important because the standards of the use or disposal of sewage sludge in several member states of the European Union include the content limits of selected organic toxicants (table 1) [1].

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Table 1

Limits of organic compound and dioxin concentration  
in land-applied sewage sludge accepted by  
some of the EU member states

Organic compounds	Maximum concentration mg/kg (dry weight basis)
AOX <sup>1</sup>	500
LAS <sup>2</sup>	2600
DEHP <sup>3</sup>	100
NPE <sup>4</sup>	50
PAH <sup>5</sup>	6
PCB <sup>6</sup>	0.8
PCDD/F <sup>7</sup>	100 ngTEQ/kg dry weight

<sup>1</sup> Sum of organic halogen derivative compounds adsorbable onto activated carbon.

<sup>2</sup> Alkylbenzenesulphonians.

<sup>3</sup> Di (2-ethylhexyl) phthalates.

<sup>4</sup> Compounds containing nonylphenol substances and oxyethylphenol compounds.

<sup>5</sup> Sum of polycyclic aromatic hydrocarbons.

<sup>6</sup> Polychlorobiphenyls.

<sup>7</sup> Polychlorodibenzodioxins/furans.

This paper discusses model experiments concerning the migration process of organic halogen compounds from the sludge into the liquid phase. *p*-chlorophenol was used as a model substance to evaluate the migration of organic halogens, depending on the *p*-chlorophenol concentration as well as some physicochemical factors such as UV radiation, aeration, temperature and pH changes in the liquid phase.

*p*-chlorophenol is reported to be commonly found in industrial wastewater [7], [9], [10], and accordingly, in sewage sludge. Being readily soluble in water (27 g/dm<sup>3</sup>/20 °C), the contaminant is expected to migrate easily from the sludge into the liquid phase. *p*-chlorophenol is an adsorbable organic halogen (AOX), thus to assess the migration rate, it was essential to measure the AOX concentration in the liquid phase at equilibrium with the sludge.

## 2. MATERIALS AND METHODS

The material under study was treated sewage sludge (P<sub>0</sub>) from a plant at Sitkówka near Kielce. The facility receives wastewater of both municipal and industrial origin, 85% and 15% respectively, which is then treated by anaerobic digestion. As is seen from table 2, the sludge can be recycled to arable land.

Table 2

## Sludge characteristics

Parameter	Unit	Value
pH		8.2
Dry matter	%	17.99
Organic substance	% d.w.	59.01
Total nitrogen	g/kg d.w.	284
Ammonium nitrogen	g/kg d.w.	43.6
Total phosphorus	g/kg d.w.	21.3
Calcium	% d.w.	0.48
Magnesium	% d.w.	0.19
Lead	mg/kg d.w.	8.9
Cadmium	mg/kg d.w.	0.5
Mercury	mg/kg d.w.	0.01
Nickel	mg/kg d.w.	19
Zinc	mg/kg d.w.	955
Copper	mg/kg d.w.	19.5
Chromium	mg/kg d.w.	28
AOX	mg Cl/kg d.w.	110

The experiment was designed as follows. *p*-chlorophenol was added to fresh sludge ( $P_0$ ) in the following amounts: 100, 200, 300, 400, and 500 mg Cl/kg (dry weight basis), thus the samples were denoted by  $P_1$ ,  $P_2$ ,  $P_3$ ,  $P_4$ , and  $P_5$ , respectively. The sludge samples,  $P_1$ – $P_5$ , 3 g each, were immersed in 25 cm<sup>3</sup> of distilled water and shaken for 1 hour. The liquid phase was separated mechanically by applying a centrifugal separator. Then, the concentration of AOXs in the solution over the sludge was determined.

At that point, the sludge containing 500 mg Cl/kg (dry weight basis) of *p*-chlorophenol ( $P_5$ ) was exposed to the following processes simulating the conditions under which the sludge may be applied to arable land:

- changeable pH of the liquid phase ranging from 4.16 to 8.12; during the test HNO<sub>3</sub> or NaOH should be added;
- UV radiation in the wavelength range of  $250 < \lambda < 280$  nm; 1 hour exposure;
- aeration in the form of barbotage for 1 hour, the flow intensity being 50 dm<sup>3</sup>/h;
- temperature ranging from –20 °C to +15 °C; the temperature effect was measured after nine freezing–thawing cycles in an air-conditioned chamber;
- conditioning at a room temperature of 20 °C and humidity of 60% for 24 hours.

The effect of each factor was analyzed. The testing involved immersing the sludge samples in distilled water, the proportion being 3 g of sludge per 25 cm<sup>3</sup> of H<sub>2</sub>O, and shaking them for 1 hour. The liquid phase was separated mechanically using a centrifugal separator. Then, the concentration of AOXs in the solution over the sludge was determined.

The sludge was measured for the *p*-chlorophenol concentration in the liquid phase using the AOX value in accordance with the Polish Standard PN-EN 1485 and employing a Behr-CI 10 analyzer and an SE Behr Labor Technik sorption column.

Additionally, the microstructure of the sewage sludge exposed to low temperatures was examined under an Olympus stereoscopic microscope equipped with a camera.

### 3. RESULTS AND DISCUSSION

A fresh sewage sludge under analysis was reported to have pH 8.2 (alkaline reaction) and a low content of heavy metals. The amount of organic halogen compounds measured with the AOX value did not exceed 110 mg Cl/kg d.w. (table 2). The amount of *p*-chlorophenol added to the sludge to trace the migration of organic halogen compounds from the sewage sludge into the liquid phase ranged from 100 to 500 mg Cl/kg d.w. Table 3 shows the AOX values measured in the liquid phase, the results being dependent on the amount of *p*-chlorophenol added to the sludge.

Table 3

AOX values in the liquid phase, depending on the amount of *p*-chlorophenol in the sludge

Amount of <i>p</i> -chlorophenol added to the sludge, mg Cl/kg d.w.	100	200	300	400	500
AOX concentration in the liquid phase, mg Cl/dm <sup>3</sup>	0.834	1.864	3.110	4.520	5.734

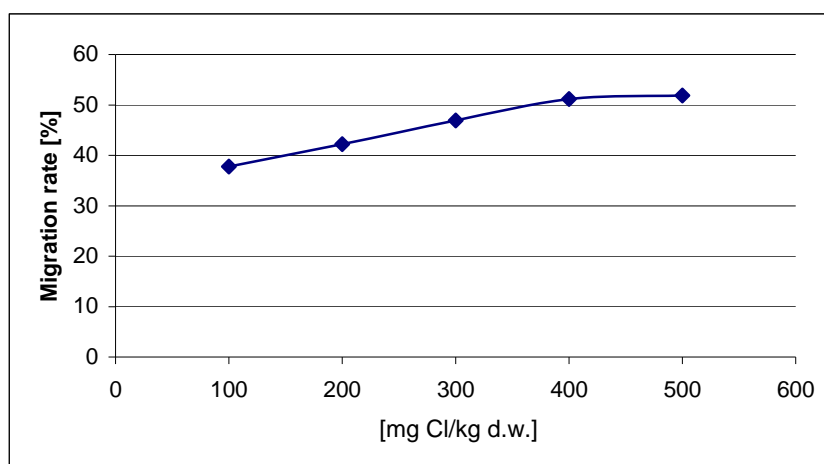


Fig. 1. Relationship between the efficiency of *p*-chlorophenol migration from the sludge to the liquid phase and its concentration in the sludge

The AOX values are proportional to the concentration of *p*-chlorophenol in the sludge. They range from 0.834 mg Cl/dm<sup>3</sup> at the *p*-chlorophenol concentration of 100 mg Cl/kg d.w. to 5.734 mg Cl/dm<sup>3</sup> at the concentration of 500 mg Cl/kg d.w. As shown in figure 1, there is no significant change in the *p*-chlorophenol migration rate. The rate, which can be defined in per cents as the mass ratio of chlorine in the liquid phase (25 cm<sup>3</sup>) to chlorine in the sludge sample (3 g), ranged from 39% to 52%. The results suggest that under the predetermined conditions only a portion of the compound added to the sludge is permanently bounded; the rest is free to transfer into the liquid phase, which is due to its ready solubility and the application of the mechanical process of shaking.

Subsequently, the sludge samples with 500 mg Cl/kg d.w. of *p*-chlorophenol (P<sub>5</sub>) were exposed to the selected physical and chemical processes. Again, they were immersed in distilled water and shaken for 1 hour. Table 4 presents the AOX values determined at the liquid phase and the calculated rate of the AOX migration.

Table 4

AOXs in the liquid phase and the *p*-chlorophenol migration rate, depending on the factor acting on the sludge (P<sub>5</sub>)

Physicochemical treatment of the sludge		AOXs in the liquid phase (mg Cl/dm <sup>3</sup> )	AOX migration rate (%)
pH	4.16	5.724	51.8
	6.22	5.734	51.9
	8.12	6.146	55.7
Aeration		6.182	56.0
Exposure to UV radiation		5.946	53.8
Freezing cycles		4.316	39.1
Conditioning		4.420	40.0

Based on the results given in Table 4, one can conclude that an increase in acidity slightly inhibits the migration of *p*-chlorophenol. At pH 8.12, the AOX value was 6.146 mg Cl/dm<sup>3</sup>, while at pH 4.16, it was 5.724 mg Cl/dm<sup>3</sup>. The migration rate did not change much, either. It was 55.7% and 51.8 %, at pH 8.12 and 4.16, respectively. A slight impact on the migration of *p*-chlorophenol, permanently bounded with the sludge, was observed after exposure of the latter to UV radiation or aeration. The migration rate was 56.0 and 53.8%, respectively. An exception was the influence of low temperatures reported after applying several freezing–thawing cycles. There were changes in the consistency and structure of the sludge both relating to the water bonding by the sludge particles (figure 2).

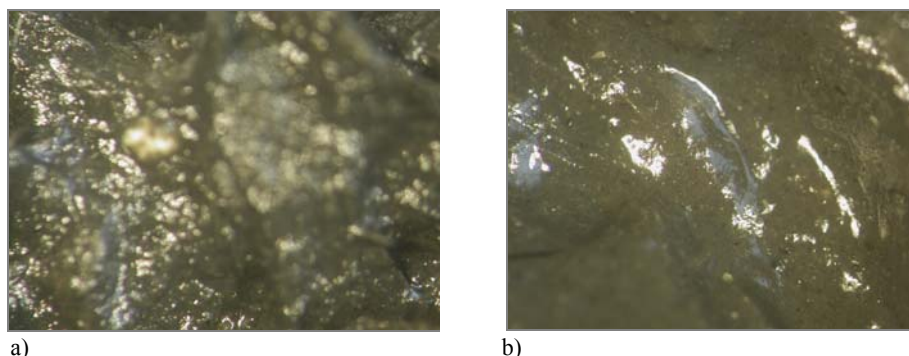


Fig. 2. Sludge surface microstructure, magnified 25×:  
a) sludge before the physicochemical treatment, b) sludge subjected to several freezing–thawing cycles

Figure 2 shows the images of sewage sludge surface microstructure. The sludge samples not subjected to physicochemical processes were characterized by plastic consistency. Water present in the sludge was bounded by capillary and adhesive forces between the sludge particles – bright points uniformly distributed over the whole area (figure 2a). Repeated freezing–thawing cycles caused changes in the sludge consistency. It became amorphous, greasy and muddy, because water was no longer held in the sludge by the capillary forces and formed irregular clusters on the surface (figure 2b). It is assumed that freezing gives rise to pressure changes in the sludge pores, this creating perfect conditions for *p*-chlorophenol desorption from the sludge to the air. As a result, its concentration in the sludge decreases, and so do the migration rate and the AOX value determined in the liquid phase. They are equal to 39.1% and 4.316 mg Cl/dm<sup>3</sup>, respectively. Samples P<sub>5</sub> were conditioned for 24 hours at a temperature of 20 °C and humidity of 60%, which resulted in *p*-chlorophenol vaporization, and, accordingly a decrease in the AOX concentration and migration rate.

#### 4. CONCLUSIONS

The following conclusions were formulated:

- The AOX concentration determined in the liquid phase was reported to be proportional to the amount of *p*-chlorophenol applied to the sludge.
- An increase in the acidity of the liquid phase decreased the transition of organic halogen compounds from sewage sludge to the liquid phase.
- Physicochemical processes such as aeration, exposure to UV radiation did not have strong impact on the *p*-chlorophenol migration from the sludge into the liquid phase.
- Low temperatures resulting from repeated freezing–thawing affected the *p*-chlorophenol migration considerably; they were responsible also for a different way of water binding with the sludge, which caused a decrease in the migration rate.

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OCENA STOPNIA MIGRACJI ZWIĄZKÓW CHLOROWCOORGANICZNYCH  
Z OSADÓW ŚCIEKOWYCH DO FAZY WODNEJ

W użytkowanych przyrodniczo osadach ściekowych obecne są toksyczne związki organiczne takie jak: WWA, chlorowcopochodne organiczne, PCB i dlatego istnieje potrzeba badań zdolności przenikania tych substancji z osadów do środowiska. W prezentowanej pracy określano wpływ wybranych czynników na proces migracji związków chlorowcoorganicznych na przykładzie *p*-chlorofenolu z osadu do fazy wodnej. Stwierdzono, że największy wpływ na migrację *p*-chlorofenolu ma jego stężenie w osadzie oraz niskie temperatury, które powodują istotne zmiany w strukturze osadu.