



RISKS ON AQUATIC ENVIRONMENT RELATED TO WASTE OF PRINTED CIRCUIT BOARDS (PCBs)

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Abstract: *Integrated circuit boards are component of most Waste Electrical and Electronic Equipment (WEEE). These are generated worldwide at an alert rhythm and their recycling is done to a small extent (about 20%). The paper presents an experimental simulation of the presence of printed circuit board waste (PCBs), from end-of-life computers, in three aquatic environments with different pH (pH 4.00, pH 5.63 and pH 8.00). After stagnation for 17 weeks, values of the concentrations of heavy metals released by the PCBs in the solutions were obtained. These indicated that the presence of these boards in aquatic media may impair water quality by inducing moderate risks for surface water and lower risks for groundwater bodies. Heavy metals such as copper and lead, especially in acidic and neutral environments, fell into the worst quality class for surface water and exceeding of the maximum allowable value for the reference groundwater body (ROS012) were recorded for copper in the acid and neutral initial solutions.*

1. INTRODUCTION

The printed circuit board (PCB) is a flat, rigid and insulating material with two complementary functions: one for fixing electronic components and the other for providing reliable electrical connections. Thin geometrically conductive structures (rectangles, squares, circles) function as interconnections or connecting points of components [1].

Printed circuit boards (PCBs) are considered hazardous waste and they are part of most of the Waste Electrical and Electronic Equipment (WEEE) being about 3-6% by weight of the total amount of WEEE. PCB contains about 28% metals and almost 70% non-metallic materials [2, 3, 4].

WEEEs are regulated in Europe by Directive 2012/19/EU and implicitly, by transposition, in Romania by GEO no. 5/2015 on waste electrical and electronic equipment [5, 6]. In over 66% countries worldwide WEEE are managed under specific regulations [7].

Although in most countries there are systems for the selective collection of waste electrical and electronic equipment from households, some of them end up being dumped together with other municipal waste on landfills, thus leading to contamination risk of environmental factors, especially surface water and groundwater. The solution is to apply the principles of the circular economy to prolong the life of the product, to recover and recycle this waste as much as possible to save natural resources and minimize the disposal of waste [8].

Globally, statistics indicate a WEEE generation of 6.1 kg/inh in 2016, compared to 5.8 kg/inh generated in 2014 [7]. The report by Balde et al., (2017) indicates a sharp increase in WEEE given that the recycling rate is quite low [7]. Of the 44.7 million tons (Mt) of electrical and electronic equipment waste generated worldwide, only 20% was recycled by appropriate methods [7]. In Europe, in 2018, an average of 8.9 kg/inh was collected, and 45% of Member States reached or exceeded the collection target and 4 other countries were very close to this performance. The largest quantities collected were recorded in countries such as: Sweden (14.2 kg/inh.), Austria (13.2 kg/inh.) and the smallest quantities were collected in countries such as: Romania (2.4 kg/inh), Lithuania (5.1 kg/inh) [9]. Romania has failed to reach the target of 45% of the average amount of EEE placed on the market in the previous 3 years [10].

Compared to the global average recycling of WEEE, the European WEEE recycling rate is higher. Therefore, in the period 2011-2018, the total WEEE collected improved from 3.0 to 4.0 million tons (+30.9%), the total WEEE treated increased from 3.3 to 3.9 million tons (+19.5%), total WEEE recovered increased from 2.7 to 3.6 million tons (+30.3%) and total WEEE recycled and ready for reuse increased from 2.6 to 3.2 million tons (+26.2%) [9].

In order to assess the risks of heavy metal contamination posed by printed circuit board wastes on environmental factors and especially on aquatic ones, several printed circuit boards from end-of-life computers were used to make a simulation of the reactivity conditions of the respective components in three aquatic environments with various pH: an acidic environment, one that simulates the rainwater and an alkaline one. The releasing of heavy metals was mainly pursued and the results were compared with the maximum allowed values provided by the Romanian legislation for surface water and groundwater.

2. MATERIALS AND METHOD

2.1 Preparation of printed circuit board samples

In order to test the releasing conditions of some heavy metals such as zinc, copper, lead, cadmium and arsenic, contained in the printed circuit boards, such components taken from various end-of-life computers were used (*fig.1*). After their separation, they were previously crushed and brought to a size of 1-4 cm.

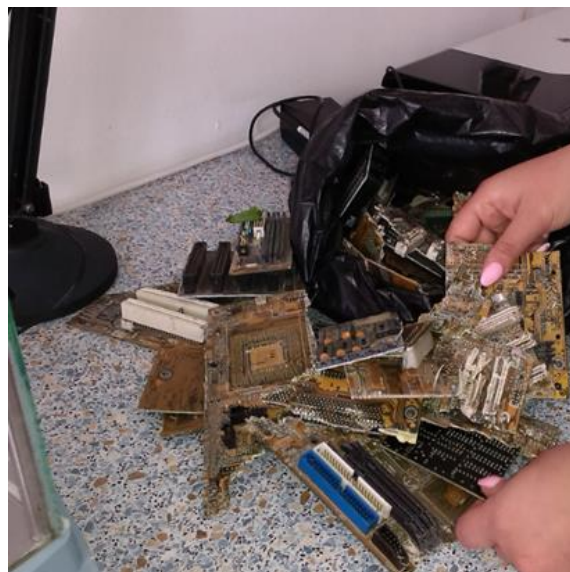


Fig. 1 Fractions of printed circuit board (PCBs)

In order to carry out the experimental part, the fragments of plates with integrated circuit were weighed so that 9 equal quantities could be obtained for their immersion in containers with solutions (3 replicates each) having three different pHs, thus simulating different liquid contact media. :

- alkaline medium, pH 8.00 (potassium hydroxide solution);
- natural environment, consisting of rainwater, pH 5.63
- acidic medium, pH 4.00 (glacial acetic acid).

The symbolization of the samples was as follows:

- For the sample with pH 4.00 the containers were marked with PI and replicates with a, b, c.
- For the sample with pH 5.63 the containers were marked with PII and replicates with a, b, c.

- For the sample with pH 8.00 the containers were marked with PIII and replicates with a, b, c.

The test of contacting the solutions with the PCBs was carried out in a ratio of 1:10 (mass of the boards to the volume of the solution) for 17 weeks, under controlled environmental conditions. The ambient temperature was kept constant at 20 ± 4 °C.

Thus, 9 individual samples were obtained, monitored at intervals of 7 days.

After 17 weeks, the solutions in each sample were subjected to the determination of pH and heavy metals released from the immersed material.

3. RESULTS AND DISCUSSION

3.1 pH reaction of contact solutions

The pH of the solutions was measured at the beginning and the end of the experiment. This was determined using a WTW laboratory pH meter type 740.

It was observed that at the end of the experiment the pH of the solutions was higher than the initial one. Surprisingly, the PI sample (with initial pH 4.00) had an average pH above 9.0. Stagnation of PCBs in solutions with pH similar to rainwater (pH = 5.63) generated pH values above 7.00, in the case of the solution with initial pH 8.00, pH with an average value slightly above 10 (fig. 2).

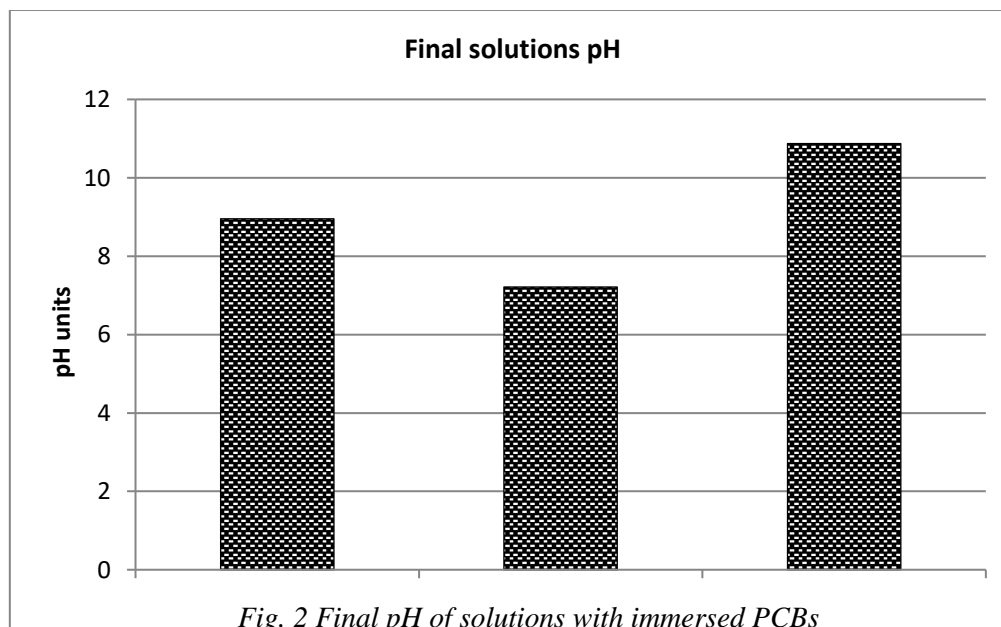


Fig. 2 Final pH of solutions with immersed PCBs

3.2 Determination of heavy metal content in solutions

At the end of the test period, after homogenization of the solutions, a volume of solution was collected from each of the three replicates (a, b, c) corresponding to each type of solution, so that the content of heavy metals in the mixed solution sample was determined.

Figure 3 shows an enhanced change in the color of the solution containing the printed circuit boards after 17 weeks of contact.

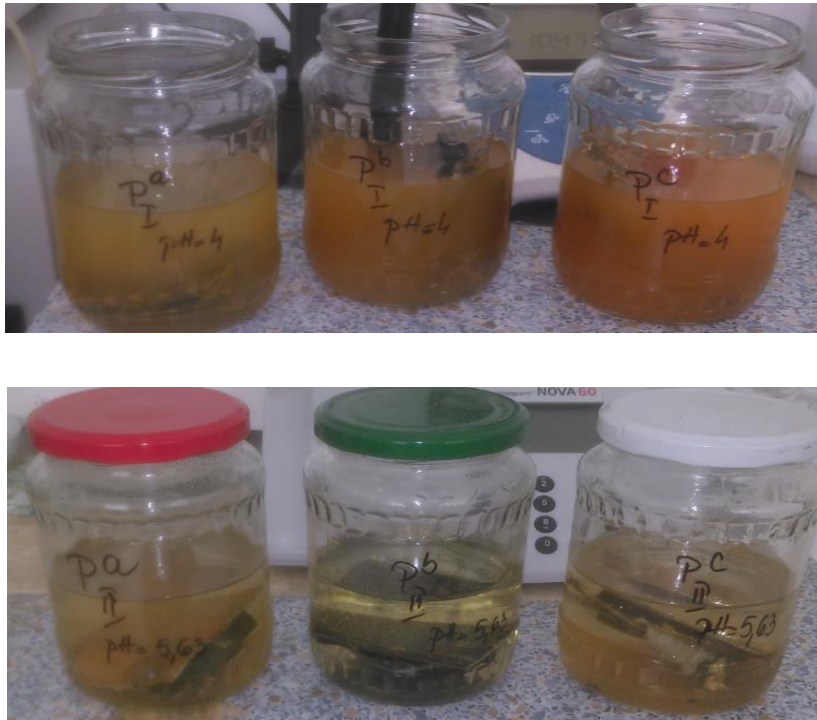


Fig. 3 The containers with solutions after 17 weeks

The sampled solutions were mineralized with regal water (HNO_3 : HCl = 1: 3), according to the standard SR EN ISO 15587-1: 2003- „Water quality. Mineralization for the determination of water elements. Part 1: Mineralization with regal water. ” [11], thus being prepared for the determination of metals of interest: zinc, copper, lead, cadmium and arsenic.

The metals were determined by flame atomic absorption spectrophotometry and graphite furnace, using an AAnalyst 700 atomic absorption spectrometer, manufactured by Perkin Elmer. The atomic absorption spectrometry analytical technique was performed on calibration curves, with the correlation factor $R^2 \geq 0.950$, made from reference solutions with traceability to NIST (manufacturer Merck).

The values of the metal concentrations in the experimental solutions were compared with the limit values allowed for the surface waters provided by Order no. 161/2006 [12] (Table 1). It should be mentioned that quality class I refers to the best water and class V, to the most depreciated.

Table 1 Maximum allowable concentrations of metals of interest in surface waters [12]

Metal	M.U.	Surface water quality class				
		I	II	III	IV	V
Copper	$\mu\text{g/l}$	100	200	500	1000	>1000
Lead	$\mu\text{g/l}$	5	10	25	50	>100
Cadmium	$\mu\text{g/l}$	0.5	1	2	5	>5
Arsenic	$\mu\text{g/l}$	10	20	50	100	>100

Assuming the existence of extremely permeable geological layers, which would allow the penetration of solutions with the determined concentrations, entirely in the groundwater, these concentrations were reported to the maximum allowed concentrations for the ROSO 12 groundwater body, belonging to the Someș-Tisa river basin. 621 of 2014 [13] (Table 2).

Table 2 Maximum allowed concentrations of metals of interest in the body of water ROSO 12 [13]

Water body	Zinc	Copper	Lead	Cadmium	Arsenic
	mg/l				
ROSO12	5	0.1	0.2	0.005	0.01

Arsenic was the only metal of interest for which the method of determination was not sufficiently sensitive. The resulting values were less than $0.5 \mu\text{g/l}$, which corresponds to the detection limit of the method.

Zinc was identified in all samples (P I, P II, P III). In the case of surface water (table 1) it was classified in quality class III for all three samples (*fig. 4*). Also, its concentration was much below the maximum allowable limit of 5 mg Zn/l in the case of the reference groundwater body (Table 2).

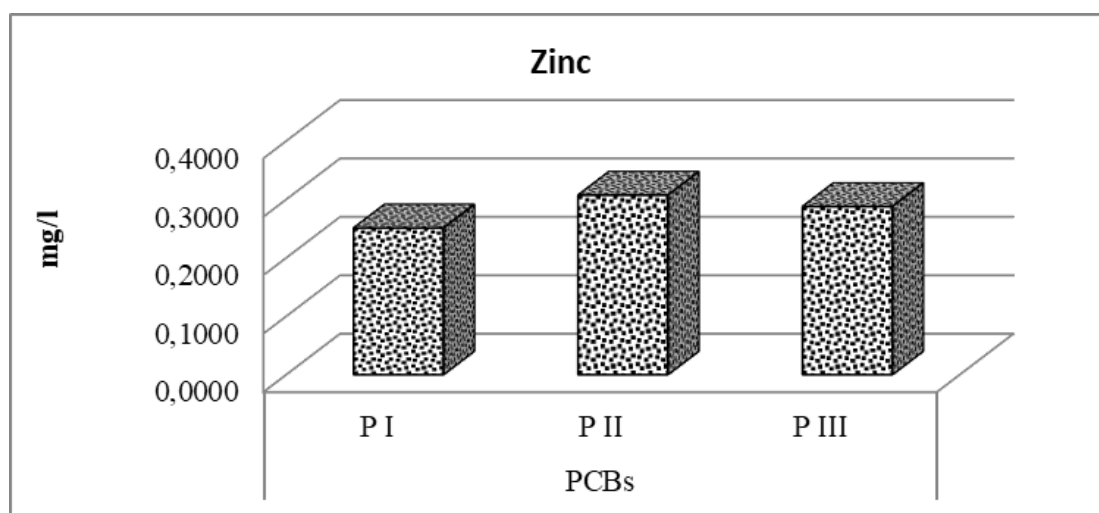


Fig. 4 Zinc concentration in solutions with PCBs

In the case of copper, regarding the quality of surface water, the concentration determined from the PIII solution fell into quality class I and the concentration of copper from samples PI and PII were much higher, falling into class V quality (table 1, *fig. 5*).

For the copper from sample PIII, it is noted that it falls within the maximum limit allowed for the reference groundwater body, but in the case of samples P I and P II the values obtained exceeded the maximum limit allowed by Order 621/2014 [13] (table 2, *fig. 5*).

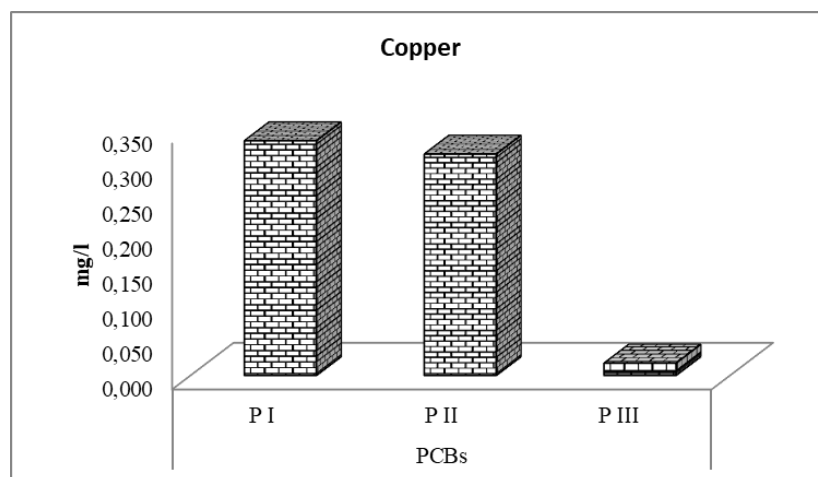


Fig. 5 Copper concentration in solutions with PCBs

The lead concentration in all three samples fell into V quality class of surface water (Table 1, *fig. 6*). Compared to the maximum allowed values for the reference groundwater body, the lead was below the maximum allowed limit (Table 2, *fig.6*).

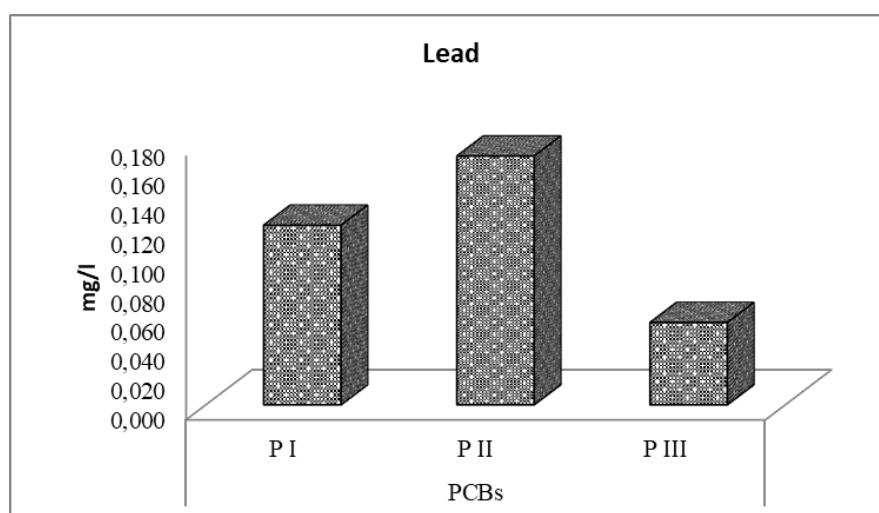


Fig. 6 Lead concentration in solutions with PCBs

The cadmium in the PIII sample was below the detection limit of the determination equipment. The cadmium concentration in the PI sample was in the II quality class of the surface water and the one in the PIII sample was in the III quality class for surface water (Table

1, *fig. 7*). Compared to the maximum allowed value for the reference groundwater body, it was noticed that all the values obtained were below this value (Table 2, *fig. 7*).

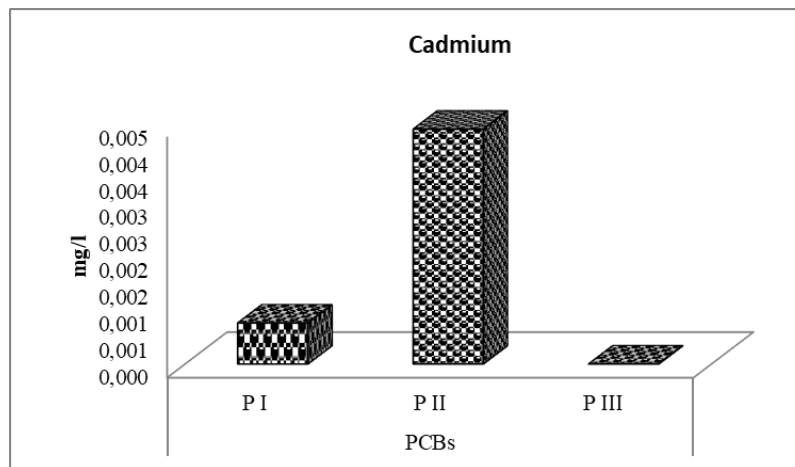


Fig. 7 Cadmium concentration in solutions with PCBs

4. CONCLUSIONS

As integrated circuit boards are components of most categories of WEEE, an experiment was performed to observe their chemistry in the aquatic environment. In this sense, integrated circuit boards were taken from several obsolete computers, which after a previous crushing and weighing were grouped into 9 equal parts. Separately, 9 containers with three pH solutions (pH 4.00, pH 5.63 and pH 8.00) were prepared to simulate different aquatic environments: acid, rainwater and alkaline. Fragmented plates and 1:10 solution were introduced into each container. After 17 weeks, the pH of the solutions and the concentration of heavy metals were determined: zinc, copper, lead, cadmium and arsenic. The values obtained were compared with the reference values for both surface water and groundwater. Thus, the zinc in the final solution was classified for all samples (PI, PII and PIII) in the class III of quality for surface water and below the maximum allowed for groundwater. In the case of copper, its value in the PIII test was in the class I of quality for the surface water and that one in the PI and PII samples was in the V quality class. The copper in samples PI and PII exceeded the maximum allowable value for the reference groundwater body while the copper concentration in sample PIII was below this limit. Lead, in all three PI, PII and PIII samples, was in the V class of quality for surface water and below the permissible limit for the reference groundwater body (ROSO12).

The cadmium in the PI sample was classified in the II quality class for surface water and the one in the PII, in the III quality class for surface waters. The cadmium in both PI and PII samples was below the maximum permissible groundwater limit. In the case of the PIII test, the value read by the device was below the detection limit. The same was the case for arsenic, the concentration of which was below the limit of reading equipment detection.

The experimental results indicate a moderate risk of the presence of PCBs in the aquatic environment for a period of 17 weeks. The metals with the highest incidence are: copper and lead and in a less share zinc and cadmium. Regarding the risk for groundwater, it can be stated that it is lower and can be conditioned by the geological and morphological structure of the area.

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