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The removal of trace metals at the wastewater treatment plant of Psyttalia

G. FIRFILIONIS[1], V. PARASKEVOPOULOU[1], G. VILIOTI[2] and M. DASSENAKIS[1]

[1] University of Athens, Department of Chemistry,
Laboratory of Environmental Chemistry,
Panepistimioupoli Zografou, 15771, Athens, Greece

[2] EYDAP, Laboratory Department of Psyttalia Wastewater Treatment Plant,
Akrokeramos, 18600-Keratsini, Greece

e-mail: edasenak@cc.uoa.gr

Abstract

The present study investigates the levels of trace metals in the input and output of the Psyttalia wastewater treatment plant, as well as the removal of the various trace metal forms (dissolved, particulate) during primary sedimentation. The trace metals determined were: Pb, Cd, Cu, Zn, Cr, and Ni. The experimental procedure included the collection and analysis of inflow and outflow samples. Dissolved and particulate forms were separated by filtration through 0.45 and 8 μm Millipore filters and trace metals were determined using atomic absorption spectrometry. The results indicate that particulate matter consists mainly of large particles (>8 μm) and the sedimentation process is more effective in their removal in contrast to smaller particles. The removal of trace metals during primary sedimentation follows the decreasing sequence: Particulate metal in large particles > Particulate metal in small particles > Dissolved metal. Concerning the various metals the removal follows the sequence: Pb ≅ Cu>Zn ≅ Cr>Cd>Ni. The quantities of trace metals that are discharged to the sea through the outflow pipes of the Psyttalia treatment plant follow the decreasing sequence: Zn >> Cr > Cu > Ni > Pb > Cd.

Keywords: Trace metals; Psyttalia; Wastewater primary treatment; Removal Efficiency.

Introduction

The wastewater treatment plant of Athens, situated on the small island of Psyttalia, in the Saronicos Gulf began its operation in 1995. About 700000 m^3 of wastewater are daily subjected to primary sedimentation.

The reduction of the pollution load entering the Saronicos Gulf has already contributed to signs of improvement in its ecosystem, which is expected to be further enhanced, after completion of the second stage of the Psyttalia works currently under construction (VILLIOTI *et al.*, 2000).

The treatment plant in full operation will achieve maximum capacity in the year 2026 and the mean volume of wastewater to be treated daily will be 966000 m^3 (VILLIOTI, 1998).

Figure 1 presents a map of the Saronicos Gulf with the Island of Psyttalia marked.

According to the EU Directive 91/271/EEC, the term 'urban wastewater' means domestic wastewater or the mixture of domestic wastewater with industrial wastewater and/or run-off rainwater. The term 'primary treatment' means the treatment of urban wastewater by a physical and/or chemical process involving settlement of suspended solids, or other processes in which the BOD_5 and the total suspended solids of the incoming wastewater are reduced by at least 20% and 50% respectively before discharge (EU Directive 91/271, 1991). Such primary treatment systems operate in various large cities around the world, i.e. San Diego, Montreal.

The decrease of BOD, suspended solids and total nitrogen after the primary treatment at Psyttalia is shown in Table 1, as well as the projected decrease after the operation of the secondary treatment plant (VILLIOTI & DASSENAKIS 1999; VILLIOTI *et al.,* 2003).

The treatment procedure of urban wastewater in Psyttalia includes the following steps (VILLIOTI, 1998):

1. Pre-treatment, that takes place in Akrokeramos at Keratsini on the coast of Attiki. It includes screening of wastewater for the removal of large debris, grit removal of inorganic particles larger than 200 μm in 6

Fig. 1: Map of Saronicos Gulf.

Table 1
% Removal of chemical and physical parameters after treatment.

	% Removal	
	Primary Treatment	**Secondary Treatment**
BOD_5	40	>90
Suspended Solids	64	90
Total Nitrogen	11.7	80-90

aerated grit chambers and finally application of an odour control system since Akrokeramos is near a residential area.

2. Transport to Psyttalia through underwater pipes.

3. Primary sedimentation in 6 aerated rectangular sedimentation tanks. The hydraulic detention time ranges from 0.56 to 1.12 h (HALLER, 1995).

4. After sedimentation the effluent is discharged into the Saronicos Gulf through two 4 km pipes at a depth of about 60 m.

The treatment of sewage sludge includes pre-thickening, with 3 gravity thickeners, mesophilic anaerobic digestion (30-35 °C), post-thickening for further reduction of volume, dewatering with belt-filter-presses and finally transportation to the landfill of Ano Liossia where the sludge is deposited. Figure 2 presents the pertinent flow-sheet (VILLIOTI *et al.* 2001).

The main sources of trace metals in urban wastewater are mentioned in the EU report 'Pollutants in urban wastewater and sewage sludge' (2001). It has been calculated that about 60-70% of the contribution of trace metals to wastewater comes from the products of human metabolism. Other sources of trace metals in wastewater are:

Pb: pipes, batteries, traffic, cosmetics, paints.

Cd: batteries, paints, photography, detergents, rainwater, platings, car-repair shops.

Cu: pipes, pesticides, pigments, wood preservatives, anti-fouling paints, electronics, platings.

Ni: food packaging, batteries, protective coatings, platings, catalysts.

Cr: alloys, preservatives, tanning, dyeing.

Zn: pesticides, wood preservatives, deodorants, cosmetics, medicines, paints, food supplements, alloys, elastics, batteries, construction materials.

The removal of trace metals after primary and secondary treatment of urban wastewater is summarised in Table 2 (EU, 2001).

The aims of the present study were:

a) to determine the percentage of Pb, Cu, Cd, Zn, Cr, Ni, that is retained during primary sedimentation of the produced sewage sludge.

b) to determine the percentage that is discharged into the sea, and

c) to elucidate the distribution of the above mentioned trace metals between the various forms.

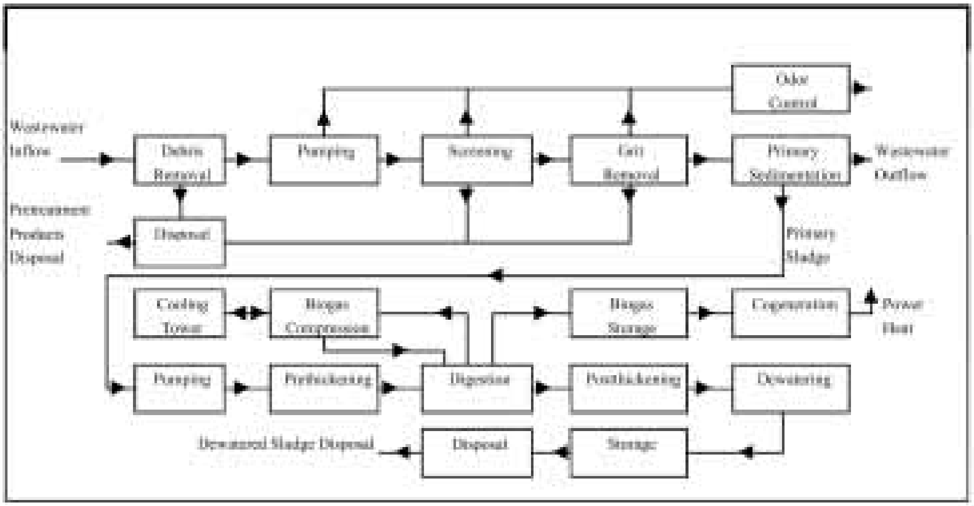

Fig. 2: Psyttalia Waste Water Treatment Plant flow-sheet.

Table 2
% Retention of trace metals after treatment of urban wastewater.

Treatment	% retention for trace metals in the sewage sludge after treatment					
	Ni	Cd	Cr	Zn	Pb	Cu
Primary	24	40	40	50	50	50
Secondary	40	40	40	40	>50	40

Materials and Methods

Samples were collected with automatic refrigerated samplers (the samples are flow proportional) on a weekly basis for 15 weeks. The IN samples were collected before the sedimentation tanks and the OUT samples were collected after sedimentation and before discharge into the sea. Each sample represents the daily composite mean inflow to the treatment plant and outflow to the sea (KEITH, 1991).

The samples were successively filtered through pre-weighed mixed cellulose Millipore filters with pore diameter of 8 and 0.45 μm. In trace metal analysis cellulose membrane and polycarbonate filters are commonly used. We chose Millipore cellulose filters because they have the following desirable characteristics: a) uniform and reproducible pore size, b) very low metal content and thus low risk for contamination, c) the residue after acid digestion is negligible, d) easy filtration, and e) relatively low cost. The filters with pore size 0.45 μm are widely used for the separation of 'dissolved-soluble' and particulate metals. Furthermore the particles with diameter over 8 μm (the maximum commercially available Millipore cellulose filters) present high settling rate and do not remain in suspension for a long time. In particular the settling velocities of silt particles (10μm) and clay particles (1μm) are 0.025 $cm \cdot s^{-1}$ and 0.00025 $cm \cdot s^{-1}$ respectively. (SALOMONS & FÖRSTNER 1984, GRANT GROSS, 1977).

The particles retained on the 8 μm filter will be subsequently mentioned as LP fraction (large particles) and the particles retained on the 0.45μm filter as SP fraction (small particles).

The filtered samples were acidified with HNO_3 and stored at 4 °C until analysis. The filters were dried and weighed to determine the mass of suspended solids. The filters were then digested in screw-capped Teflon beakers with conc. HNO_3 on a hot plate.

Trace metals were measured with atomic absorption spectroscopy using the spectrometers VARIAN SpectrAA 200 (flame AAS) and VARIAN SpectrAA 640Z (graphite furnace AAS) (APHA 1998).

Results

Particulate mass-Particle size distribution

The concentrations of suspended solids varied significantly during the studied period, but in all samples the large particles (LP) prevailed. There was also a wide range in the removal of suspended particles. However the sedimentation process is more effective in the removal of the LP fraction (Fig. 3). After the primary sedimentation there was a decrease in the LP fraction percentage from 93 to 84%

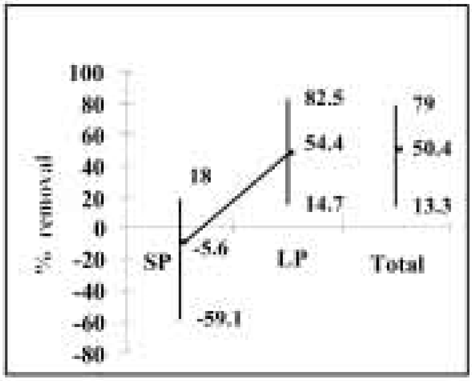

Fig. 3: Removal of suspended particles during primary sedimentation.

and an increase to the small particles (SP) fraction percentage from 7 to 16% (Fig. 4). The negative values of small particles removal in Figure 3 indicate that during the treatment of effluents small particles are produced either by break up of large particles or by formation of insoluble compounds.

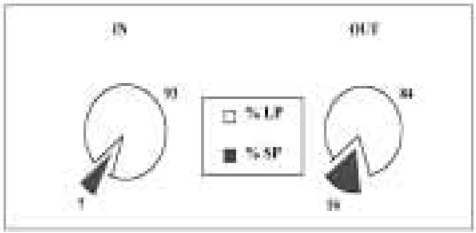

Fig. 4: Distribution of particulate matter.

Removal of trace metals

During primary sedimentation trace metals are removed from the incoming wastewater, as is apparent from the lower concentrations in the OUT samples due to retention in the sewage sludge (Table 3). Figure 5 presents the percentage of removal for all three forms of the trace metals, as well as for the total metal during primary sedimentation. The diagrams show the minimum, maximum and geometric mean removal for each of the examined trace metals. The geometric mean was chosen because the removal of trace metals did not follow normal distribution (CARAYANNIS 1978; UNEP/ MAP / (MED POL 1994).

The lowest removal was observed for dissolved Ni and the highest for particulate Pb in the LP fraction. The removal of trace metals during primary sedimentation exhibits significant variations, but generally follows the decreasing sequence: Particulate Metal in LP fraction > Particulate metal in SP fraction > Dissolved metal.

Despite the wide range of removal from sample to sample the geometric mean of retention corresponds to the mean values provided by the EU for primary treatment of urban wastewater (Zn 50%, Cu 52%, Ni 24%, Cr 40%, Pb 56%, Cd 40%). (EU, 2001).

Main forms of trace metals

The mean percentages of each metal form, both in the IN and OUT samples, are presented in Figure 6. For Cr, Pb and Cu, the

Table 3
Mean trace metal concentrations.

	Pb (μg/l)		**Cd (μg/l)**	
Form	IN	OUT	IN	OUT
Dissolved	4.78	2.80	0.18	0.13
Particulate>8μm	20.7	8.55	0.23	0.11
Particulate>0.45μm	2.27	1.16	0.07	0.04
Total	28.6	13.1	0.56	0.34
	Cu (μg/l)		**Ni (μg/l)**	
Form	IN	OUT	IN	OUT
Dissolved	8.45	5.94	24.2	16.5
Particulate>8μm	35.3	15.1	6.90	3.45
Particulate>0.45μm	6.56	3.84	0.74	0.38
Total	52.2	26.0	32.2	21.0
	Cr (μg/l)		**Zn (mg/l)**	
Form	IN	OUT	IN	OUT
Dissolved	14.9	9.76	0.129	0.068
Particulate>8μm	79.4	41.8	0.248	0.158
Particulate>0.45μm	5.93	3.12	0.046	0.028
Total	102.1	56.9	0.456	0.268

dominant form is particulate metal (>75%). In the case of Zn and Cd the percentage of particulate metals is between 45-70%. This is because Pb and Cu are generally more strongly bound to inorganic and organic absorbents than Zn and Cd (SALOMONS & FÖRSTNER 1984). In the case of Ni the dissolved form prevails (>70%) due to the high solubility of Ni compounds in wastewaters (EU, 2001).

After the primary sedimentation we observed a decrease in the percentage of trace metals in the LP fraction, a slight increase in dissolved metal percentages and relative stability in the percentage of metals in the SP fraction.

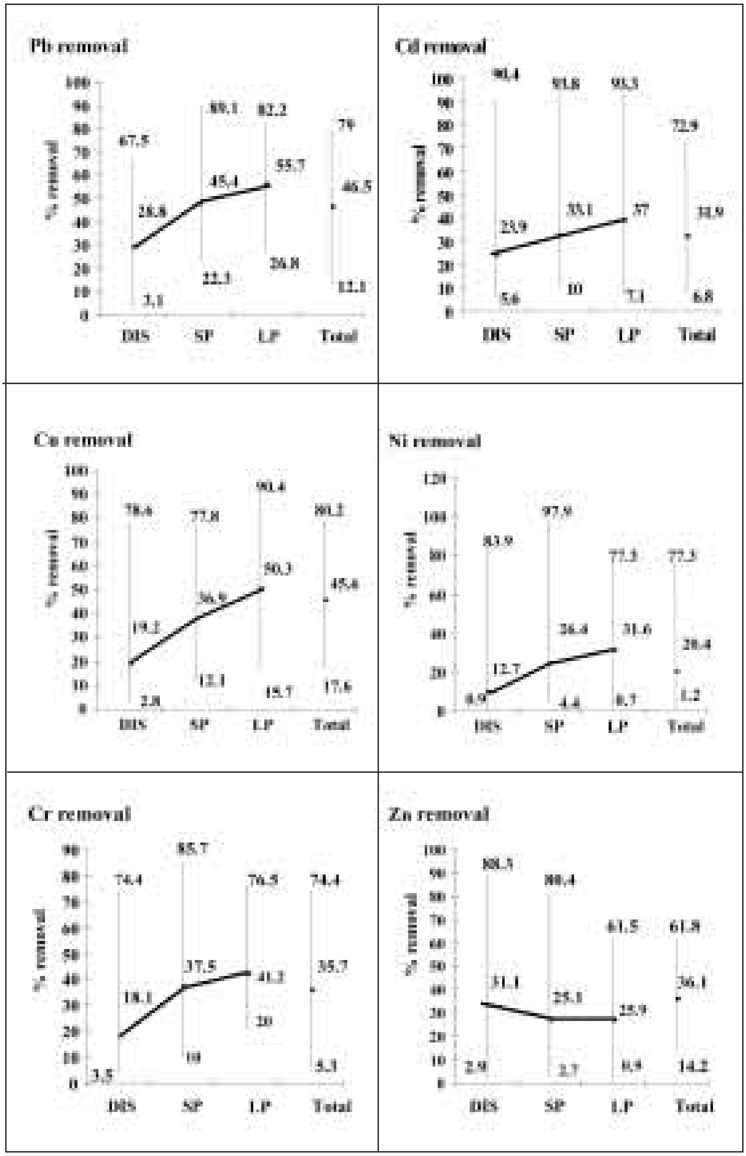

Fig. 5: Trace metal removal during treatment.

Trace metal content of particles

The content of particles in trace metals is expressed as w/w concentration (Fig. 7.) In the IN samples the metal content of small particles is higher than the content of large particles. Small particles are mainly clay minerals and organic material that have a high metal content due to increased absorbing ability (RABBITI 1983, SALOMONS & FÖRSTNER 1984). It is apparent from the comparison of IN and OUT values that the sedimentation process led to the decrease of metal content in small particles (SP). This decreasing trend in metal content was not observed in the LP fraction.

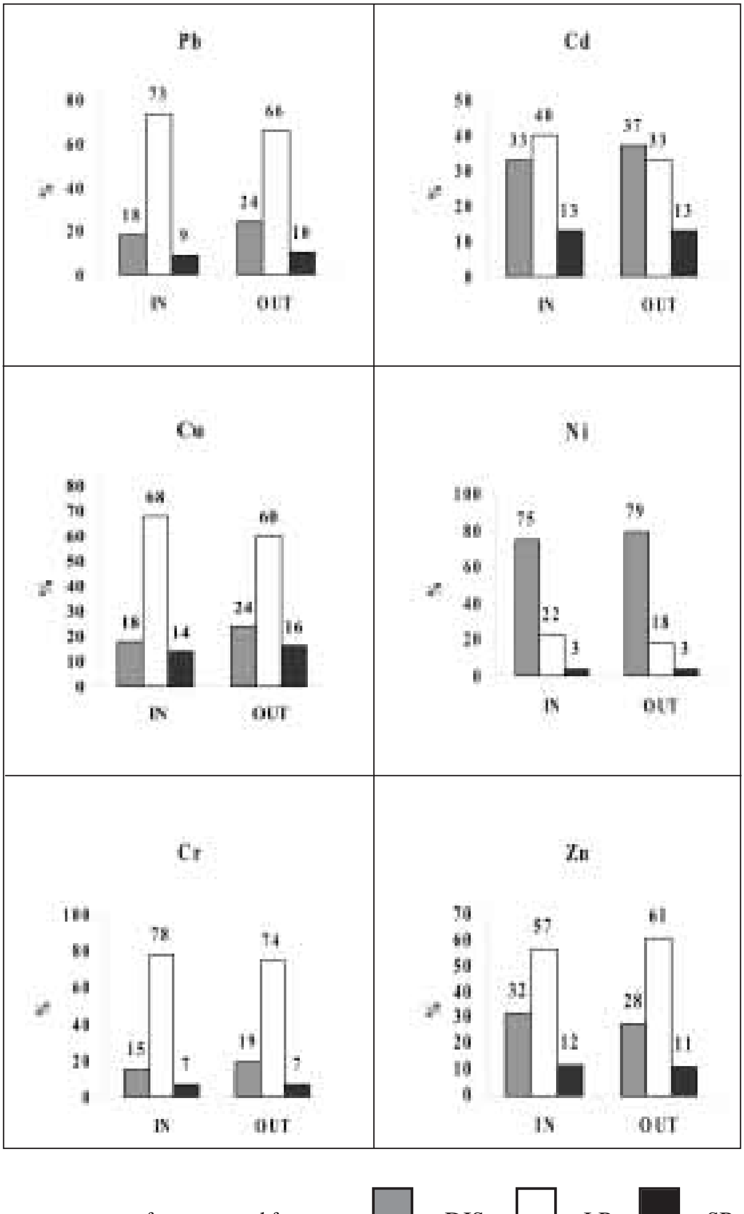

Fig. 6: Mean percentages of trace metal forms

Discharge of trace metals into the sea

Despite the fact that during wastewater treatment there is significant retention of trace metals in sewage sludge, the remaining amount that is discharged into the sea is considerable. The average daily quantity of trace metals discharged into the sea, can be calculated as follows:

$$Q_{Me}\,(kg/d) = 10^{-3} \times C_{Me}\,(\mu g/l) \times F\,(m^3/d),$$

where C_{Me} (μg/l) is the metal in the daily representative sample and F the wastewater flow rate.

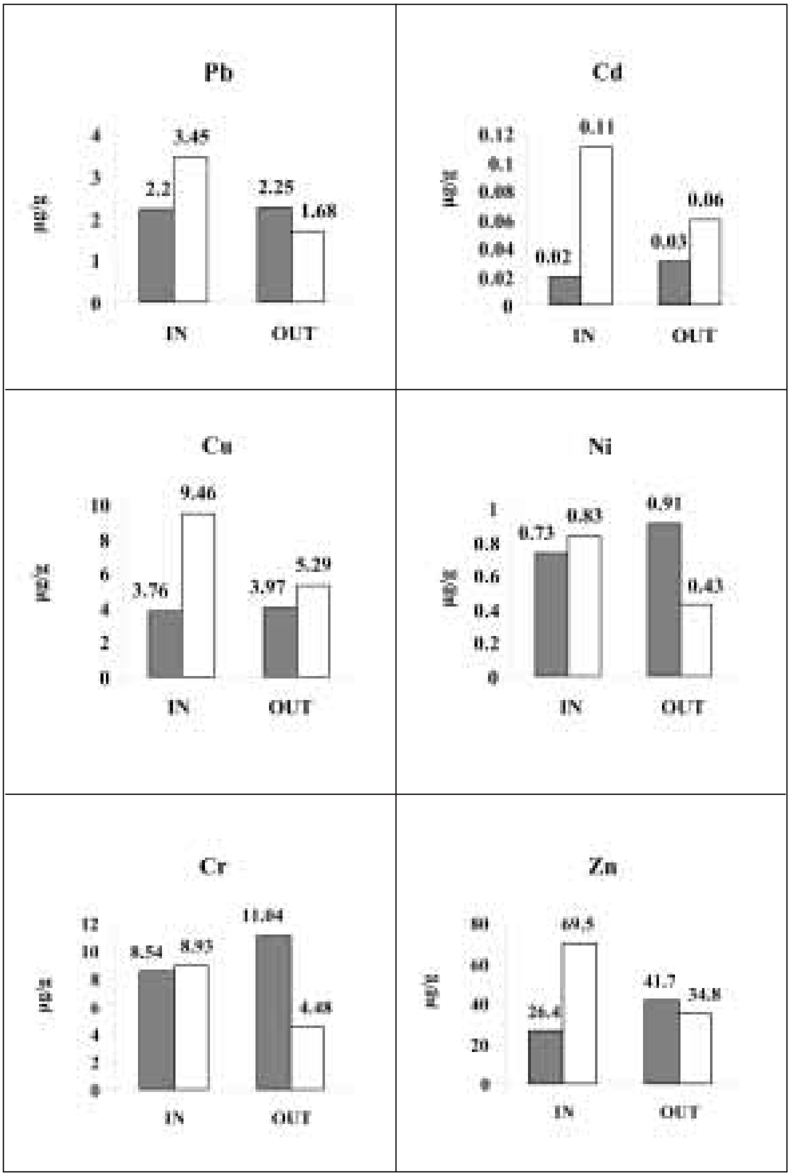

Fig. 7: Metal content of particulate matter (μg/g) LP SP

The Q_{Me} was calculated for each sampling date, taking into account the mean daily outflow of wastewater into the sea, which is 700000 m^3. The calculation was applied to all three forms of the trace metals and total metal. The geometric means of discharge for every trace metal form are shown in Table 4.

The quantities of trace metals that are discharged into the sea through the outflow pipes of the Psyttalia treatment plant follow the decreasing sequence: Zn > Cr > Cu > Ni > Pb > Cd.

Concerning the forms of trace metals, Pb, Cu, Cr and Zn end up in the sea mainly connected to large particles while Ni and Cd in the dissolved form. Figure 8 presents the percentages of the forms in which the examined trace metals are discharged into the sea.

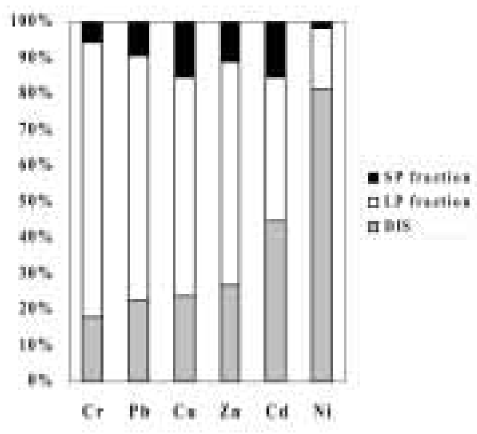

Fig. 8: Percentages of trace metal forms discharged to the sea.

Discussion

The general observations from the present research can be summarised as follows:

There were large variations in pollutant concentrations in incoming and outgoing effluents and in removal efficiency of the primary sedimentation. These variations can be attributed to the complexity of the mixture of the Athens wastewater (domestic, industrial, run-off) and the temporal variations of its composition. (VILLIOTI, 1998)

The sedimentation process was found more effective in the removal of the LP fraction, which represents the higher percentage of particulate matter.

The removal efficiencies of trace metals during primary sedimentation generally follow the decreasing sequence: Particulate metal in LP fraction > Particulate metal in SP fraction > Dissolved metal.

Concerning the various metals the removal follows the sequence: Pb ≅ Cu>Zn ≅ Cr>Cd>Ni.

The metal content of the LP fraction remains relatively stable during primary sedimentation, indicating a lower degree of participation of this form in the physico-chemical and biological processes taking place in the sedimentation tanks.

Most chemical processes mainly affect small particles and dissolved forms. Thus the observation of reduction in metal content in the SP fraction during the treatment process (Fig. 7) and the increase in the percentage of dissolved metals in the OUT samples (Fig. 6) indicate metal transfer from the SP fraction

Table 4
Quantities of trace metal discharge to the sea (in kg/d).

	Pb	Cu	Cr	Zn	Cd	Ni
DIS form	1.96	4.16	6.83	47.6	0.088	11.6
LP form	5.98	10.6	29.3	110.5	0.079	2.42
SP form	0.81	2.69	2.19	19.3	0.030	0.27
Total	7.20	18.2	39.7	182.8	0.240	14.7

to the dissolved fraction. The small net removal of dissolved metals in the treatment process (Fig. 5) is a result of the co-existence of two contrasting procedures, absorption of dissolved metals in the removed sewage sludge and release of metals from small particles. The hypoxic conditions in the sedimentation tanks favour the processes described above. (SCOULLOS *et al.*, 1986)

The quantities of trace metals that are discharged into the sea through the outflow pipes of the Psyttalia treatment plant follow the decreasing sequence: Zn >> Cr > Cu > Ni > Pb > Cd. It is important to mention that the quantity of Zn discharged into the sea is much higher than the quantities of all the other metals, which can be attributed to the wide use of zinc in domestic, industrial and other applications.

Comparison of Psyttalia to the Point Loma wastewater treatment plant of San Diego, California, USA, which is also a primary treatment facility processing 704000 m^3 of wastewater daily, showed that both facilities discharge similar quantities of dissolved Zn and Pb into the sea, while Psyttalia discharges higher quantities of Ni and Cr and Point Loma discharges higher quantities of Cu and Cd (RACO-RANDS 1997; VILLAESCUSA-CELAYA 2000).

Concerning the forms in which the examined trace metals are discharged into the sea: a) for Pb, Cu, Cr and Zn between 60-70% of the discharged metal is in the LP fraction. b) for Ni about 80% enters the sea in the dissolved phase and c) for Cd the percentages of dissolved LP fraction are similar and around 35%. It is accepted that the physical, chemical and biological characteristics of receiving waters (temperature, pH, salinity, alkalinity, dissolved oxygen, nature and amount of suspended matter) affect the speciation of trace metals, thus modifying their bioavailability and toxicity (GAGNON 2003; LUOMA 1983). The main percentage of metal content in small particles is non-lattice held, in contrast to larger particles, because of their increased absorbing capacity. It is also known that exchangeable metals in non-lattice positions are bioavailable. (SALOMONS & FÖRSTNER 1984). Therefore the discharge of trace metals, mainly in the LP particulate phase, is a positive aspect of the Psyttalia treatment system, because the ecotoxicologic impact on the marine ecosystem of the Saronicos Gulf in general is probably lower. However, the high percentage of dissolved Cd discharged, despite the generally small total quantity of the metal entering the sea needs to be examined further, since Cd is a highly toxic metal and a priority pollutant in the Mediterranean.

There are no data available regarding the transformations of metal species after their discharge into the Saronicos Gulf from the Psyttalia treatment plant. However, it is possible that an amount of particulate metals will be transferred to the dissolved phase due to the ion-exchange activity of the main seawater cations (K^+, Na^+, Ca^{2+}) (DASSENAKIS *et al.*, 1997; SCOULLOS *et al.*, 1996).

Conclusions

The operation of the wastewater treatment plant of Psyttalia can be characterized as satisfactory for the examined trace metals because the levels of removal correspond to the European mean values reported for primary treatment and are compoarable with similar plants all over the world. The upcoming operation of the secondary treatment at Psyttalia will certainly affect the quantities and species of trace metals discharged into the Saronicos Gulf, therefore the results of the present study will be very useful for future comparison.

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