

ASSESSING THE HEAVY METAL CONTENT OF SUSPENDED PARTICULATE MATTER AND OF GROUNDWATER OCCURRING IN THE AREA OF THE FUTURE WEAK- AND - MEDIUM RADIOACTIVE WASTE REPOSITORY SALIGNY – ROMANIA

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Abstract: By means of atomic absorption spectrometry with atomization in flame and in graphite oven, the concentration of heavy metals (Cu, Zn, Ni, Cr, Cd and Pb) has been determined in suspended particulate matter and in groundwater occurring in the area of the future weak- and medium-radioactive waste repository at Saligny-Romania. Experimental results have shown that for certain heavy metals (for instance Zn and Ni), which in the dissolved phase occurred in concentrations that ranged close to, or below the detection limit of the utilized methods, quantitative determinations could be nonetheless obtained for the corresponding contents in the suspended particulate matter (for Zn: 611.7-40527.7 ppb and for Ni: 80.7-3053.7 ppb). It was thus outlined the important part that the suspended particulate matter played in the pollutants transfer in natural aqueous environments.

Keywords: heavy metals, suspended particulate matter, groundwater, waste repository, Saligny

1. INTRODUCTION

Among the elements with elevated toxic potential that occur in the environment, the heavy metals are the most toxic inorganic pollutants. Their impact is quite severe, since in this respect, the underground aquatic ecosystems have only a poor self-cleaning capacity. In particular, heavy metals accumulate in the water, in the sediments and in the particulate matter. It is nowadays unanimously recognized the fact that the suspended particulate matter (SPM) plays an important role in the contaminants transport: most elements with elevated toxic potential are partly or almost entirely carry away by SPM (Fetweis et al., 2007; Minaberry & Gordillo, 2007). A multitude of complex chemical and biogeochemical processes, as well as existing hydrogeological settings contribute to heavy metals becoming more concentrated by adhering to these active surfaces (Audry et al., 2006; Minaberry & Gordillo, 2010). Consequently, it is quite frequent that heavy metals which in the water samples are present just at (or below) the detection limit of the analytical methods, become quantitatively detectable when occurring on the SPM; this latter circumstance

requires corresponding appropriate investigations to be included in the monitoring programs. There are two different ways for assessing the concentrations of heavy metals attached to SPM, namely a direct, and an indirect one. The direct assessment methods consist in separating the suspensions, by means of filtering, after which the separated matter is digested and analyzed as a general rule (Ödman et al., 1999, 2006; Marin et al., 2010a). The indirect assessment consists in separately analyzing the filtered and the unfiltered water sample, and in ascribing the difference in concentration between the two analyzes to the concentration of the element attached to the SPM (Cidu & Frau, 2009; Gammons et al., 2005; Pokrovsky & Schott, 2002; Cortecchi et al., 2009; Guéguen et al., 2004). A comparative study of the results obtained through the two methods has been performed by Butler et al., (2008).

In terms of concerned analytical techniques, assessments of the heavy metals contents are usually carried out by atomic spectrometry including flame (F-AAS) or graphite furnace (GF-AAS) atomic absorption spectrometry, inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF) (Florea et al., 2005; Tudorache et al., 2010, 2011;

Matache et al., 2009; Munteanu et al., 2012; Balaban et al., 2011; Huzum et al., 2012). In addition, the AAS and ICP-MS spectrometric techniques have been successfully utilized for investigating the distribution of certain heavy metals in the dissolved phase, in the SPM and in the sediments (Vasile & Vlădescu, 2010; Campean et al., 2012; Nguyen et al., 2005; Basha et al., 2010). However, due to the high complexity of the matrices and to the low levels of the metal ions concentrations in the water samples, their separation, and also the use of a preconcentration step prior to the metal analysis are usually required. To this purpose, a multitude of separation and preconcentration procedures have been developed for trace metal ion determination, including: solid phase extractions (Tuzen et al., 2005; Liu et al., 2005; Tokaloğlu et al., 2009; Shabani et al., 2009), ion exchange (Kara et al., 2005, 2006), coprecipitation (Tokaloğlu & Yıldız, 2009) or size exclusion chromatography (Laborda et al., 2009).

At the present time in Romania there is one operational Nuclear Power Plant (NPP) at Cernavodă. The low and intermediate level radioactive waste resulted from the operation of Cernavodă NPP i.e. compactable waste, non-compactable waste, organic liquids, spent filter cartridges and the low activity spent resins, will be deposited in the Saligny Repository, planned to be built in the vicinity of the Cernavodă NPP (Niculae et al., 2009). The disposal of radioactive waste needs to be carried out in a manner that provides an acceptable level of safety and which can be demonstrated to comply with the established regulatory requirements and criteria.

The main objective of the present study was to evaluate the distribution of Cu, Zn, Cd, Pb, Cr and Ni concentrations in groundwater and in suspended particulate matter from Saligny area where the low and intermediate level radioactive wastes generated at Cernavodă Nuclear Power Plant are planned to be disposed into a future repository.

2. EXPERIMENTAL SECTION

2.1. Hydrogeological setting of the sampling sites

An area extending between the Danube and the Black Sea-Danube Channel, in close vicinity of the NPP at Cernavodă, is being currently considered for the development of a future weakly and medium active waste repository (Saligny FWMAWR). The highest elevation in this region reaches 72 m above the Black Sea level, and there is no dense network of perennial streams flowing in the area. The main surface-water bodies are the Danube-Black Sea Channel and Țibrinului Pond, the latter being located about 2 km to the north with respect to the study area. During heavy

rainfall seasons, a stream flows along Cișmelei Valley, its supply being provided by a spring which discharges from a nearby outcrop of Eocene limestone. The rocks lithology in this region is dominated by: loessoid clayey silts; loessoid silty clays; loessoid clays; red clays; Pre-Quaternary clays (consisting of kaolinitic and marly clays, glauconitic and kaolinitic sands, kaolinite clays, sands with gravel and limestone intercalations); Berriasian-age sandstone and limestone having undergone weathering and fracturing. The main aquifers in this region are: (1) Berriasian, a quasi-continuous aquifer directly connected to the Danube and to the Danube-Black Sea Channel; (2) Aptian, a discontinuous aquifer consisting of carbonate and sandy lens; (3) Eocene, an aquifer developed in limestone having the indicated age and which occurs only locally, in Cișmelei valley, and (4) the Quaternary aquifer (Danchiv et al., 2004). In terms of mineral content, in that area there occur prevalently clay minerals (such as: montmorillonite, smectite, illite, kaolinite), but also carbonate minerals (calcite, dolomite) (Durdun, 2001).

2.2. Sampling and analytical methods

In order to provide a characterization of the repository area in terms of some heavy metals concentrations, groundwater samples have been collected during November 2011 from 15 piezometric observation drillholes and 2 wells (Fig. 1). Out of a total of 17 sampling sites, the Berriasian aquifer was sampled by 8 sites (FC22, FS20, FC25, PH06, FS27, GP-C, GP-V and well B7), the Aptian aquifer by 4 sites (FC17, PH02, APT1 and APT2), the Eocene aquifer by 2 sites (PH05 and well V. Cișmelei) and Quaternary aquifer by one site (FS09), while 2 sites sampled water mixtures from several aquifers (FS21 and FS24). In all cases samples were collected using bailers in agreement with Schoenleber (2005).

When samples were being collected, a Crison PH 25 portable instrument was used in order to perform all pH measurements. The pH-meter was calibrated using two pH standard solutions purchased from CRISON: one having the pH 4.01 and the other pH 7.00. In situ temperatures have been measured by means of a Crison TM 65 portable thermometer. Water samples were filtered in situ by means of a Chromatography Research Supplies filtering system, provided with a manual Nalgene vacuum pump. Pre weighed (Kern 770-60) MF-Millipore Membrane, mixed cellulose esters of 0.45 μm porosity and of 47 mm diameter have been used for filtering. Each filtered membrane was washed in ultra-pure water before the experiment and used only once. Filtered water samples have been collected in HDPE Nalgene sampling bottles which had been previously washed with ultra-pure water. For the AAS determinations, the samples were acidified with Ultrapur®

60% nitric acid to pH 2 and stored at 4°C. The filtered membranes with the collected material have been stored in individual polystyrene Petri dishes, both during their shipment and in laboratory, in refrigerating boxes at 4°C.

The Cu and Zn concentrations in samples were determined in laboratory by F-AAS (SR ISO 2001), while the Ni, Cr, Cd, and Pb concentrations were determined in laboratory by GF-AAS (SR EN ISO 2004). The determinations were carried out with a Perkin-Elmer atomic absorption spectrometer, model AAnalyst 700, with deuterium arc background correction, equipped with an HGA-800 graphite furnace, an AS-800 autosampler (for GF-AAS) and S10 autosampler (for F-AAS). The calibration lines were traced using solutions prepared from standard solutions CertiPUR® (Merck). The methods accuracy, precision and sensitivity were tested by using the reference matters provided by Perkin-Elmer groundwater and wastewater pollution control certified reference materials (Trace Metals I-15 elements-Part No. N9300211, Trace Metals II-3 elements-Part No. N9300212 and Trace Metals III-6 elements-Part No. N9300213). All the solutions were prepared with ultra-pure water (TKA Ultra Pure System GenPure, electric resistance 18.2 MΩ×cm).

In F-AAS determinations (for Cu and Zn), all measurements were carried out in an air/acetylene flame, at flow rates of 17 and 2.0 L/min, with a 10 cm long slot-burner head (Table 1). In GF-AAS determinations (for Ni, Cr, Cd, and Pb), pyrolytically coated graphite tubes with integrated platforms (Perkin-Elmer catalog No. B3001262) were used (Table 2). The graphite furnace temperature programs were carried out according to the manufacturer recommendations. In most cases the water samples were analyzed directly, with an injected sample volume of 20 µL. The performance of the employed analytical procedures was determined according to the International Union of Pure and Applied Chemistry (IUPAC) (Thompson et al., 1999, 2002) EURACHEM (Ellison et al., 2000) recommendations (Tables 3, 4). The filtered membranes digestion has been performed in laboratory in accordance with the specifications indicated by Marin et al., (2010a). Thus, filtered membranes were dried at room temperature in a laminar flow hood overnight and then weighed. The filters were then digested at room temperature for 48 h with 5 ml of 1:1 (v/v) solutions Ultrapur 60% HNO₃ and 30% HCl (Merck).

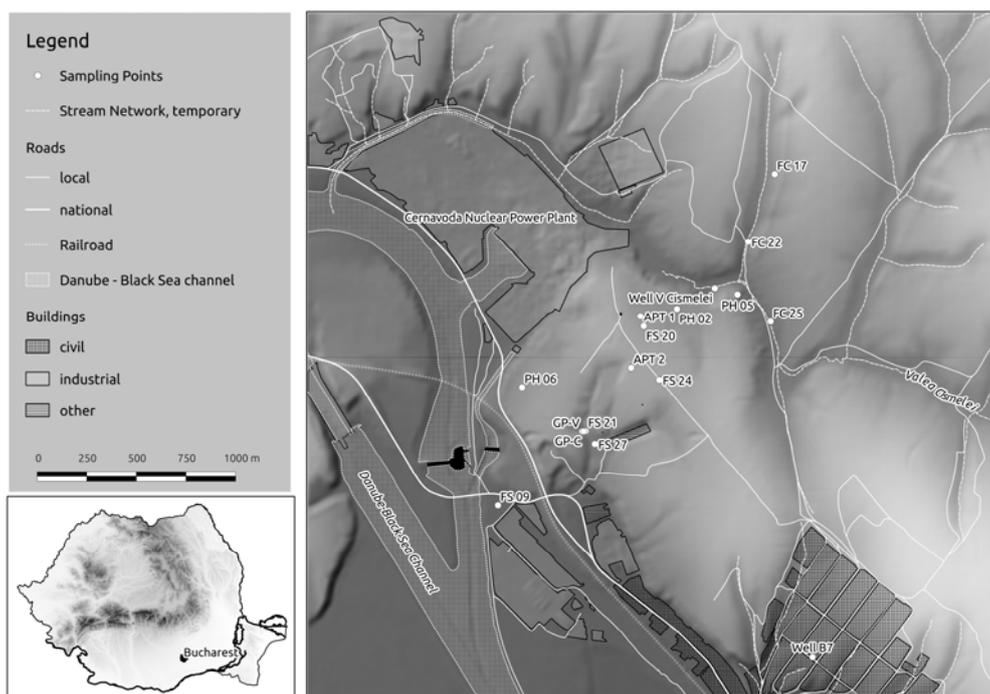


Figure 1 – Location map indicating groundwater sampling sites

Table 1 – The operating instrumental condition for the F-AAS methods

Parameter	ELEMENT	Cu	Zn
Lamp		HCL	EDL
Wavelength (nm)		324.8	213.9
Slit (nm)		0.7	0.7
Calibration curve		Linear	Linear
Calibration points (mg/L)		0.5; 1.0; 2.0	0.1; 0.3; 0.6

Table 2 – The operating instrumental condition for GF-AAS methods

ELEMENT	Cd	Pb	Cr	Ni
Parameter				
Lamp	HCL	HCL	HCL	HCL
Wavelength (nm)	228.8	283.3	357.9	232.0
Slit (nm)	0.7	0.7	0.7	0.2
Calibration curve	Nonlinear	Linear	Linear	Linear
Calibration points (ug/L)	0.5; 1.5; 3.0	3; 9; 18	2; 6; 12	5; 15; 30
Matrix modifier (5 uL)	0.3% Pd + 0.2%	4.0% NH ₄ H ₂ PO ₄	1.0%	1.0%

Table 3 – Performance parameters for F-AAS methods

ELEMENT	Cu	Zn
Parameter		
Limit of detection	<i>n</i>	10
	mg/L	0.019
	<i>St. dev.</i>	0.003
Repeatability	<i>n</i>	8
	<i>St. dev.</i>	0.087 (at 0.5mg/L)
Reproducibility	<i>n</i>	19
	<i>St. dev.</i>	0.008 (at 0.5mg/L)
Trueness ("bias")	<i>n</i>	8
	%	0.425 (at 0.5mg/L)
Experimental recovery	%	89.1–104.7

Table 4 – Performance parameters for GF-AAS methods

ELEMENT	Cd	Pb	Cr	Ni
Parameter				
Limit of detection	<i>n</i>	17	16	14
	ug/L	0.019	0.742	0.898
	<i>St. dev.</i>	0.004	0.150	0.179
Repeatability	<i>n</i>	7	5	6
	<i>St. dev.</i>	0.053 (at 2 ug/L)	0.340 (at 10 ug/L)	0.129 (at 10 ug/L)
Reproducibility	<i>n</i>	15	9	22
	<i>St. dev.</i>	0.100 (at 2 ug/L)	0.530 (at 10 ug/L)	0.418 (at 10 ug/L)
Trueness ("bias")	<i>n</i>	7	7	10
	%	1.078 (at 2 ug/L)	6.607 (at 10 ug/L)	1.365 (at 10 ug/L)
Experimental recovery	%	93.2–107.4	92.5–104.8	87.5–105.7

The digest solutions were mixed occasionally during the digestion time. A 2 mL aliquot of the digest solution (not including any visible solid) was diluted to 50 mL with ultrapure water and analyzed by AAS. This process was repeated for duplicate unused filters and the average elemental content in the filter blanks was subtracted from the sample results.

3. RESULTS AND DISCUSSION

In table 5 there are indicated the results of the heavy metal content determinations for the groundwater samples collected from the studied area. For 7 sampling sites, there have been performed quantitative determinations of the heavy metal contents associated to the SPM. The results are indicated in table 6. For the groundwater samples there have been recorded pH values ranging between 7.23 and 10.65, while the sampled groundwater temperatures ranged between 10.3°C and 11.5°C. No clear relationship between dissolved and particulate Cu, Zn, Cd, Cr, Ni and Pb concentrations and any physical parameters (e.g., pH and temperature) was observed.

3.1. Copper and Chromium

Out of all heavy metals having been analyzed in the aqueous phase, the Cu and Cr contents determined for the sample collected from the drillhole APT2 displayed the highest values, namely 315.1 ppb Cu and 245.9 ppb Cr. Those large concentrations are interpreted to be a result of the fact that in the year 2006, a tracer experiment was performed by injecting salts of Cu (II) and Cr (III) in the drillhole APT2. Excessive Cu concentrations associated to SPM were recorded in the samples collected from the well B7 (18999.6 ppb) and from the drillholes APT2 (776881.6 ppb) and FS24 (156150.3 ppb). It is obvious that in the case of the APT2 drillhole, an actual adsorption on the particulate matter is not involved; in fact, there have been most probably collected the Cu (II) salts used as a tracer, and which were still not dissolved, while for the well B7 and the drillhole FS24, it might be possible that the Cu migration pathways which diverged from the injection point (the drillhole APT2) included those two sampling sites. In the case of the SPM-associated Cr, the largest concentration

(4165.9 ppb) was recorded in the particulate matter collected from the B7 well, located in Saligny village. It is most probable that this element migrated from the APT2 drillhole toward the southern part of the study area, while simultaneously there has also occurred an accumulation of deposited cinder, resulting from coal burning for domestic heating (Li et al., 2005; Huffman et al., 1993).

3.2. Cadmium

Cd is a highly mobile and toxic element and it can be easily released into the environment through weathering and leaching (Schipper et al., 2008). Its mobility in natural aqueous systems is directly influenced by temperature, pH and the carbonate ions concentration; accordingly, for the water samples collected in the month of November 2011 and for which the in-situ temperatures ranged between 10.3°C and 11.5°C, the Cd concentration levels were relatively low, between 0.042 and 0.118 ppb.

For five sampling sites (FC17, FC22, FC20, PH02 and FC25) the concentration of this metal in the dissolved phase was below the detection limit of the utilized method

(0.019 ppb). As compared to the other SPM-associated heavy metal contents, Cd associated to SPM displayed the lowest concentration levels, between 2.25 and 107.9 ppb. Similar Cd concentrations in the SPM have been determined in two coupled Mediterranean coastal ecosystems (Rossi & Jamet, 2008).

3.3. Zinc

By the method we utilized, no Zn could be detected in the aqueous phase, because the corresponding concentrations ranged below the method detection limit (42 ppb); in contrast, significant concentrations, between 611.7 and 40527.1 ppb, were determined in the case of the SPM. The adsorption of the Zn²⁺ ions on the SPM is due to certain polarization phenomena. Specifically, since no electron is left without pair in the 3d orbital of Zn²⁺, the latter displays an increased affinity for the still free anion positions in the clay sediments. Therefore, Zn was characterized by high potential mobility, as binding to highly reactive phases (Audry et al., 2006).

Table 5 – Heavy metals concentrations determined for groundwater samples collected from the Saligny FWMAWR area (concentrations are expressed as ppb)

Source	Cu	Zn	Ni	Cr	Cd	Pb
FC17	< LOD	0.789				
FC22	< LOD	10.55				
FS20	19.02	< LOD	< LOD	< LOD	< LOD	2.477
PH02	21.11	< LOD	< LOD	1.721	< LOD	< LOD
PH05	< LOD	< LOD	4.084	< LOD	0.044	138.2
FC25	< LOD	< LOD	1.918	0.933	< LOD	0.818
APT2	315.1	< LOD	< LOD	245.9	0.084	< LOD
FS21	< LOD	< LOD	< LOD	< LOD	0.071	< LOD
FS24	19.08	< LOD	< LOD	< LOD	0.118	< LOD
PH06	19.10	< LOD	< LOD	3.614	0.075	37.58
FS27	25.21	< LOD	< LOD	< LOD	0.046	1.093
GP-C	27.11	< LOD	< LOD	10.79	0.066	< LOD
GP-V	35.05	< LOD	< LOD	11.35	0.066	< LOD
APT1	19.41	< LOD	5.963	1.641	0.105	< LOD
FS9	< LOD	< LOD	< LOD	0.991	0.045	< LOD
WELL CIŞMELEI V.	< LOD	< LOD	< LOD	74.34	0.042	< LOD
WELL B7	34.04	< LOD	< LOD	0.971	0.064	< LOD

Table 6 – Concentrations of heavy metals associated to the suspended particulate matter occurring in groundwater samples collected from the Saligny FWMAWR area (concentrations are expressed as ppb)

Source	Cu	Zn	Ni	Cr	Cd	Pb
APT2	776881.6	1381.3	246.3	680.1	49.5	721.5
FS21	2386.8	718.2	708.3	292.2	41.6	893.9
FS24	156150.3	40527.1	1347.8	838.2	34.8	3997.1
FS27	499.5	611.7	80.7	34.8	2.25	2665.8
GP-C	2463.7	1116.9	317.1	483.1	2.25	122.4
GP-V	4106.3	1865.6	318.8	86.8	4.50	303.3
WELL B7	18999.6	13573.7	3053.7	4165.9	107.9	4400.5

3.4. Lead

Due to a long-time utilization of lead-containing fuels (tetraethyl-lead is added to gasoline in order to increase their octane rating), this metal frequently occurs in natural waters (Matache et al., 2009; Jalgaonkar, 2008, Marin et al., 2010b).

For example, Pb isotopic studies in the Seine River (France) have shown that almost half of the Pb transported is of anthropogenic origin (Masson et al., 2006; Audry et al., 2004). The highest Pb concentrations have been detected in the water samples collected from the wells PH05 (138.2 ppb), PH06 (37.58 ppb) and FC22 (10.55 ppb). As these sites occur in the proximity of local and national roads, such elevated concentrations must be ascribed to emissions from vehicles which travel across the study area. In order to explain why there was no lead detected in the dissolved phase of other analyzed samples, one should take into account that: (1) having similar ionic radius lead ions can easily substitute potassium ions frequently present in the clays; (2) lead ions also compete with calcium ions to the adsorption on clays, Pb^{2+} adsorption being favored by a factor of 2 or 3 compared to Ca^{2+} . Such explanations may be invoked for the high concentrations of SPM-associated Pb detected in the drillholes FS24 (3997.1 ppb), FS27 (2665.8 ppb) and in the well B7 (4400.5 ppb).

3.5. Nickel

An evolution similar to that of Zn was also noticed in the case of Ni. The concentrations of most water samples ranged below the method detection limit (1.608 ppb), except for the samples collected from the drillholes PH05 (4.084 ppb); APT1 (5.963 ppb) and FC25 (1.918 ppb). The highest Ni content associated to the SPM has been determined for the sample collected from the well B7 (3053.7 ppb). Since the Berriasian aquifer tapped by the well B7 is subject to a continuous communication with the river Danube and with the Danube-Black Sea Channel, local pollution sources are the probable cause for the large concentration of SPM-associated Ni detected in the well B7 (Dinu, 2009). On the other hand, the presence of SPM-associated Ni in the B7 well, suggests that in natural aqueous environments, the mobility of this ion is much larger than that of Cd. These results are consistent with the heavy metals mobility in the estuarine mixing zone, for which researches have shown, based on adsorption-desorption kinetic studies (Zhang et al.,

2008), that Ni was more mobile than Cd. It therefore becomes obvious that as far as the heavy metals transport in groundwater is concerned, the SPM represents the main conveying agent (Cobelo-García et al., 2004; Coynel et al., 2007). The nature of suspended particles occurring in groundwater is highly diverse. Specifically, they may be solid fragments removed from the substratum by the flowing water, or particles generated within the very water body as a result of the latter becoming supersaturated with respect to certain components (e.g. metal oxyhydroxides), but they may be also living or decaying organisms, as well as their exudates. The active surface of those particles is the most important carrying-phase for heavy metals, being able to outpace significantly the transport by solution (Munk et al., 2002).

4. CONCLUSIONS

An assessment of the Cu, Zn, Ni, Cr, Cd and Pb contents existing in groundwater and associated SPM has been provided by the present paper, by considering samples collected in November 2011 from 15 piezometric observation drillholes and 2 wells that are situated in the area of the future weak and medium active waste repository at Saligny (Romania). The analyses were performed by means of atomic absorption spectrometry with thermal and electrothermal atomization. The results indicate that in the dissolved phase, the maximum concentrations of Cu and Cr occurred in the sample collected from the drillhole APT2 (which taps the Aptian aquifer); the maximum Cd concentration was recorded for the sample collected from the drillhole FS24 (water mixture), as for Pb, the sample collected from the drillhole PH05 (the Berriasian aquifer) displayed the maximum concentration. Most analyses of Ni contents in the dissolved phase indicated concentrations that ranged below the method detection limit, except for the samples collected from the drillholes PH05, FC25 and APT1. A similar behavior was also noticed in the case of Zn. The analysis of the SPM highlighted the very significant part played by this phase in the transport of the elements chemical species through natural aqueous environments. The presence of clays favors the occurrence of very large amounts of SPM in groundwater. Into the SPM there are accumulated and concentrated the chemical species of certain elements which in solution are present just as trace-concentrations, and so the SPM behaves as the most important vector in conveying such constituents. Accordingly, it has been possible to detect Zn in the SPM, although its presence in the dissolved phase could not be ascertained. In contrast, significant

concentrations of Cu and Cr were identified both in the SPM, and in the water samples from which the SPM separation had been performed.

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