

Original Research

Chromium Originating from Tanneries in River Sediments: a Preliminary Investigation from the Upper Dunajec River (Poland)

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Received: March 21, 2006

Accepted: June 1, 2006

Abstract

In this paper we examine the mineralogy of sediments and the distribution of chromium between particle-size classes, and describe the contaminated sediment distribution in the upper Dunajec River. No relationship between grain-size classes and Cr concentration was found in the contaminated sediments, but chromium concentration increased with decreasing grain-size in non-contaminated sediments. Fragments of leather were identified in the bottom sediments in proximity to wastewater discharges from tanneries. At each of the contaminated sites, Cr is enriched in the organic fraction of the uppermost surface sediments, while the clay fraction is relatively poor in this metal. The contamination factor in sediments is about 100.

Keywords: chromium, the Dunajec River, sediment, tannery, mineralogy

Introduction

Tanneries are one of the most prominent sources of chromium pollution to the aquatic environment. If not adequately treated, wastewater from tanneries contaminates surface water and sediments to an unacceptable level, as shown by numerous studies from Poland [1, 2], Ireland [3], Brazil [4], Mexico [5], Italy [6], Morocco [7], India [8] and many other countries.

The tanning process is carried out with the use of chromium tanning agents, principally basic chromium sulphates. As a result of proteolysis and condensation processes in water solution, these salts form a mixture of hydroxo- and aqua-complexes. The presence of sulphate radicals, showing also complexing properties, increases the stability of collagen and tannin fixations. The reaction of cationic complexes of chromium (III) with ionized carboxyl groups (COO⁻) of aspar-

ganine and glutamine acid radicals is central for the tanning process. These reactions lead to the crosslinking (coordination bonds) of collagen fibres, giving the leather its durable finish and stability [9, 10]. Chromium from tanneries is thus discharged principally as Cr(III) bound to organic and inorganic ligands [3]. At neutral or slightly basic pH, chromium is relatively immobile in tannery sludge [11]. In receiving waters, chromium is found essentially as hydroxy-complexes of low solubility associated with the particulate phase [for review see 12] and concentrates in sediments. In the proximity of tannery effluents, river sediment contains more than 1 mg Cr per g [4, 6.13].

The upper Dunajec watershed in the Carpathian Mountains is one of the most popular recreational areas in Poland and includes the recently constructed (1997) Czorsztyn Reservoir. The region, with only modest industrialization and urbanization, includes about 300 small tanneries where hide is tanned with the use of chromium compounds. Despite existing legislation and infrastruc-

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ture, such as the Sewage Treatment Plant (STP) in Nowy Targ equipped with a special line for tannery waste treatment, wastewater management is still not adequate [14–16]. Tanneries discharge pre-treated or raw wastewater into the local sewers or directly into streams. These discharges are seasonal and intermittent in character, with the highest chromium load in autumn and winter, when leather production is at its maximum [13, 16]. Chromium compounds introduced into the river are temporarily accumulated in bottom sediments. It appears that even nominally dissolved Cr(III) is largely associated with the colloidal phase [17, 18] forming polynuclear hydroxide complexes which acquire a higher molecular weight during transport [19] and can be incorporated into sediments due to colloid aggregation followed by sedimentation. The affinity of Cr(III) for the particulate phase obviously decreases its bioavailability to phytoplankton, but its high concentrations in sediments might have detrimental effects for benthic organisms and ultimately for the higher level of aquatic food chain. Surprisingly little is known about the distribution and association of Cr originating from tanneries in contaminated sediments of rivers and lakes, except some data of sequential extraction [6, 8].

The purpose of this study is to get an insight into the distribution of chromium accumulated in sediments of the Dunajec River at the contaminated sites as compared to similar sediments with natural concentrations of Cr. In particular, the identification of sediment matrix and the examination of Cr concentrations in various grain-size fractions can help to predict the mobility and bioavailability of chromium in fluvial sediments. It may also be important for the planning of monitoring strategies.

Material and Methods

Study Area

The geology of the upper Dunajec watershed is complex. The flysch formation of Carpathian units is composed

of Magura and sub-Magura shales and sandstones (Gorce Mts.) and sandstones and shales of the Zakopane and Chochołów formations. Limestones, marls, shales and sandstones represent the rocks of the Pieniny Klippen Belt [20].

The Dunajec River originates from the confluence of two main streams: the Biały Dunajec and the Czarny Dunajec (Fig. 1). The Czarny Dunajec catchment consists mainly of calcareous sedimentary rocks, while the Biały Dunajec and the Białka River, an important tributary of the Dunajec (which in turn flows into the Czorsztyn Reservoir), drain areas with sedimentary and crystalline rocks of the Tatra Mountains. The mean annual water discharges of these streams are 9.0, 5.3 and 7.0 m³s⁻¹, for the Czarny Dunajec, Biały Dunajec and Białka, respectively [21]. The mean discharge of the Dunajec downstream from the confluence of the Biały and Czarny Dunajec for the period 1951–80 was 14.5 m³s⁻¹ and at the present dam cross-section at Czorsztyn it is 23.8 m³s⁻¹ [22].

Sampling and Sample Handling

Water was sampled on 22nd November 2003 from five sites to determine the physicochemical parameters and the suspended matter (SM) content. Temperature, conductivity and pH were measured *in situ*. Samples of water with suspended matter (2 dm³) were collected from the river directly into acid pre-washed polyethylene bottles. Separation of solid particles from water was carried out using 0.45 µm Millipore membrane filters within 12 hours after sampling. The SM concentrations were determined gravimetrically with a precision of ±0.00001g.

Sediment samples were collected during the tannery production season in November 2003 and/or January 2004 at sites shown in Fig. 1. Reference sediment samples, upstream from tannery discharges, were taken from the Biały Dunajec (Ob), Czarny Dunajec (Oc) and Białka (O) rivers. Downstream from tanneries, samples were taken from a canal carrying wastewater from a small tannery to the

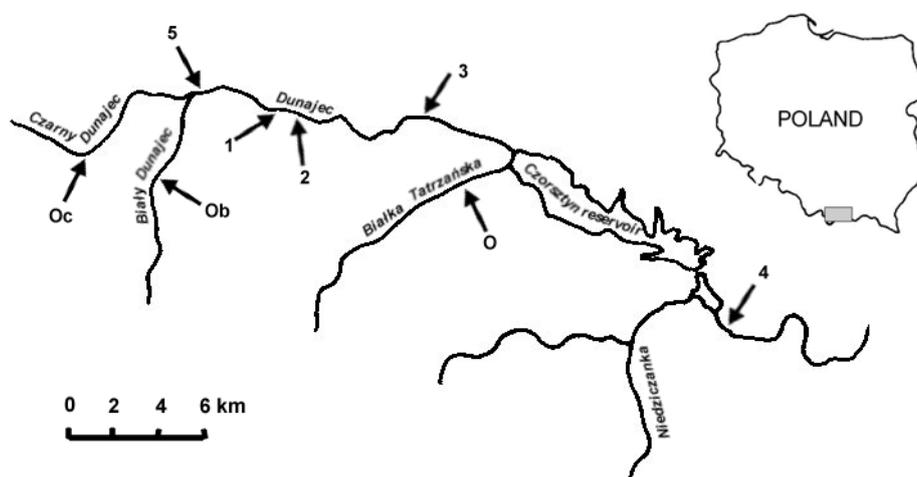


Fig. 1. Schematic map of the investigated area and location of sampling sites.

Dunajec (site 1), from the Dunajec at the village of Waksmund (site 2), at the village Harklowa just upstream from the Czorsztyn Reservoir (site 3) and at Sromowce Wyżne, downstream of the reservoir (site 4). Sample 5 represents the sludge from the STP at Nowy Targ. Samples from all sites except Ob and Oc were collected on 22nd November 2003. Additionally, sediment samples from sites O, Ob, Oc, 2 and 4 were collected on 30th January 2004. Sediments were sampled at sites where river current was slow and a thin layer of surface sediment rich in organic matter was present. This uppermost layer, sampled separately, is subsequently called surface sediment layer (SSL). The underlying more compact sediments were sampled to a depth of about 2 cm and after discarding of >2000 µm fraction are called bulk sediment (BS). Samples were placed in plastic boxes and transported to the laboratory for grain-size separation and analysis.

A sample of sewage sludge was obtained from the STP in Nowy Targ located at site 5 (Fig. 1) from a lagoon of dehydrated sludge. A specimen of tanned pig leather was obtained from a local tannery.

Separation of Sediment Grain-Size Fractions

In order to separate correctly the different grain-size fractions, the aggregates of fine clay particle should be disintegrated. For that purpose water suspensions of sediments studied were subjected to mechanical and ultrasonic treatment. The SSL samples were divided into two sub-samples. From one of them three fraction >63, 63–20 and <20 µm were quantitatively separated. Another sub-sample was introduced into the Imhoff settling cone for the separation of “organic fraction.” In fact it is not pure organic substance but a mixture of slowly settling particles, enriched in organic matter. The “organic substance” as a layer existing on the surface of suspension remains in the settling cone, while the suspension containing more readily settling particles is from the released cone. That suspension (without organic substance) is subject to preliminary treatment (mechanical and ultrasonical disintegration) and then left for sedimentation. After 8 hours (according to the rule of sedimentation) the suspension containing < 2 µm particles is taken (clay fraction).

Five size fractions were obtained from the BS samples: >2000, 2000–180, 180–63, 63–20 and <20 µm. All the separated fractions were dried at about 60–70°C and the aliquots prepared for chemical analysis.

Optical Microscopy

The BS sub-samples were fixed with polymers and thin sections prepared for observation under a polarising optical microscope (Polmi A). Mineral composition, expressed as a percentage of surface, has been estimated using jumping counter technique with 500 points counted. Thin sec-

tion photographs at partly polarized light were taken with a Nikon F90x camera using Konica VX 400 super film.

Chemical Analysis

The BS (<2000 µm fraction) were assayed with flame AAS (UNICAM 939 AA Spectrometer at the Cracow University of Technology) for Cr, Fe and Mn after extraction with concentrated HNO₃ and HClO₄ in Kjeldahl flasks according to the method described by Ostrowska *et al.* [23]. Mean analytical error was 3% and detection limit was better than 0.01 mg L⁻¹, at least significantly lower than the lowest concentration in assayed solutions.

Selected grain-size fractions from both the BS and SSL samples were digested with concentrated HNO₃ (at 130°C for 2 hours) and assayed for Cr, Fe and Mn with flame AAS (PYE UNICAM SP9) at the University of Science and Technology-AGH. The analytical error for all results was less than 5%, and the detection limit for chromium was less than 0.02 mg L⁻¹, at least significantly lower than the lowest concentration in assayed solutions. SRM 1645 River Sediment was used for indication of experiment reproducibility. The % recovery of Cr, Fe and Mn from the certified material SRM 1645 was 90, 83 and 85, respectively.

Suspended matter (SM) retained on filters was dried to a constant weight at 105°C and analyzed after acid digestion using the same procedure as for the selected sediment grain fractions.

Results and Discussion

Water and Suspended Sediments

A low temperature (5.0–6.7°C), relatively high conductivity (especially at Waksmund and Harklowa, sites 1–3), slightly alkaline pH (8.1 to 9.3) and low suspended matter concentrations (1–2 mg dm⁻³) were fairly typical for the upper Dunajec River conditions in November (Table 1). The Białka River and the Dunajec River downstream from the reservoir have a distinctly lower conductivity and the Białka River has very low SM concentration.

Sediment Grain Size and Mineral Composition

Grain-size analysis shows that samples from the surface sediment layer (SSL, Fig. 2a) are generally sandy with more than 70% of grains larger than 63 µm, although two samples from the Dunajec River (sites 2 and 4) are sandy silt (more than 50% in the fraction < 63 µm). The bulk sediments (BS, Fig. 2b) are usually coarser, except for sediments in the industrial canal draining into the Dunajec River (site 1) and in the Białka River (site O), where the BS are richer in silt than the SSL. Coarse sand is typically present at sites Ob and Oc.

Table 1. Physicochemical parameters of water samples collected on 22nd November 2003 (for site locations see Fig. 1) collected on 30th January 2004* (for site locations see Fig. 7).

Site no	Location	River	Temp. °C	pH	Conductivity $\mu\text{S cm}^{-1}$	SM mg L^{-1}
Oc*	Ludźmierz	Czarny Dunajec	0.4	8.09	594	ND
Ob*	Szaflary	Biały Dunajec	0.3	8.14	733	ND
O	Dębno	Białka	4.9	8.7	401	0.09
1	Waksmund	Canal to the Dunajec R.	6.4	8.1	1044	4.91
2	Waksmund	Dunajec	6.0	8.5	916	1.91
3	Harkłowa	Dunajec	4.9	9.3	738	1.08
4	Sromowce W.	Dunajec	6.8	8.3	555	1.48

ND = not determined

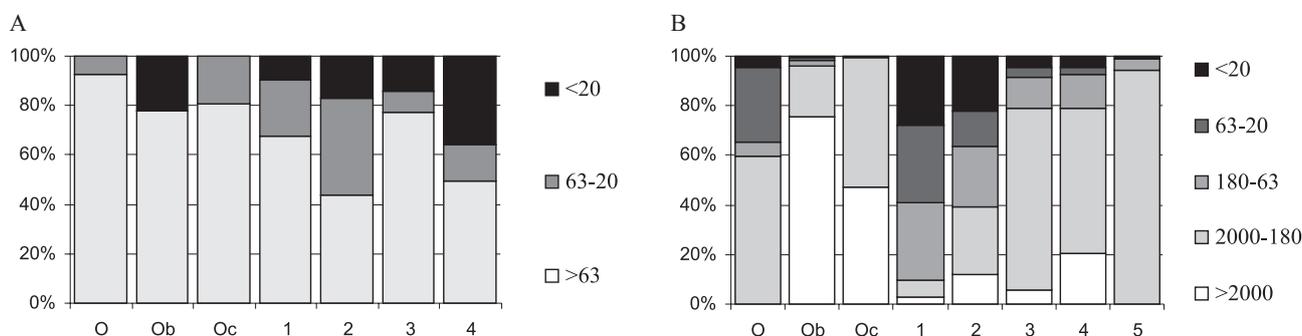


Fig. 2. Grain-size fraction in the samples from surface sediment layer – SSL (a) and bulk sediment – BS (b) from the Dunajec and Białka Rivers. See Fig. 1 for sampling sites. Sample No. 5 is the sludge from the Sewage Treatment Plant (STP) in Nowy Targ. Size classes in μm .

Optical microscopy indicated that sediment from the Białka River comprise abundant angular grains of plagioclase, quartz and mica, derived from physical weathering of crystalline rocks, and only a minor amount of organic and clay matrix. Sediments from the Dunajec River at site 2, in the region of discharges from the tanneries, have similar composition although there are more carbonates, and organic-rich clay matrix. Fragments of leather have also been identified (Fig. 3). These fragments are even more abundant in sediments from the canal (Fig. 4, site 1) used by a local tannery for the discharge of wastewater.

Grain-size analysis shows that less than 30% of the sediment particles is $< 20 \mu\text{m}$, and that there are many cemented aggregates that could not be disintegrated by the procedure applied prior to sieving. Sediments from site 4, downstream from the Czorsztyn Reservoir, are more fine-grained than those from the sites located upstream, with an exception for sediments from site 2. Needle-like amorphous particles observed in sediment from site 4 are likely to be diatom tests composed of silica (Fig. 5). These originate in the reservoir, where diatoms proliferate in spring and summer [24]. Finally, the thin section of sludge from the STP (site 5) reveals a large predominance of organic-rich clay matrix with some detrital silt-size grains and fragments of black organic detritus (Fig. 6).

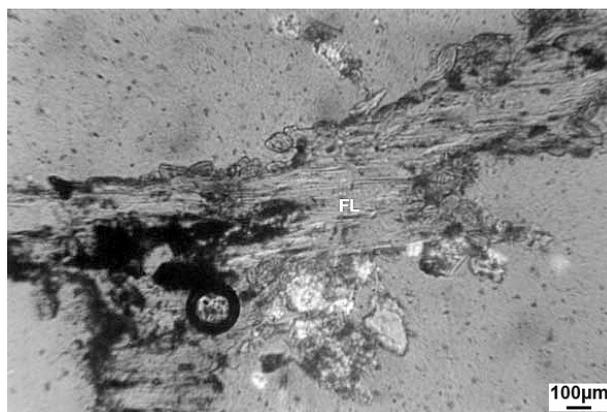


Fig. 3. Sediment from the Dunajec River (site 2). Fragment of leather (FL) with characteristic fibrous structure were occasionally found at this location and originated from tannery effluents. Thin section under optical microscope in partly polarised light. Magnification 60x.

The mineral composition of sediments, estimated from the counting of 500 points in each thin section, is given in Table 2. The dominant component of the BS is clay-organic matrix (40-64%), followed by quartz (14-42%) and carbonates. The latter are nearly absent in rivers draining crystalline

Table 2. Mineral composition of sediments (BS) determined by counting 500 points in thin sections (for sample location see Figs. 1 and 7).

Composition (% surface)	Sample							
	O	Ob	Oc	1	2	3	4	5
Organic-clay matrix	40.1	54.1	49.3	56.8	44.7	52.6	64.1	78.4
Quartz	42.0	30.1	39.7	30.8	14.1	21	19	7.7
K- feldspars	9.1	7.3	0.2	2.5	1.0	1.1	0.5	0
Plagioclase	4.9	2.1	0	0.7	0.7	0	0	0.2
Sedimentary rock fragments	0.4	2.8	5.7	0.2	0.6	0.9	0.6	0.3
Crystalline rock fragments	2.7	3.1	0.7	0	0	0	0	0
Metamorphic rock fragments	0.2	0	0.2	0.1	0	0.7	0.6	0
Muscovite	0.3	0	0.4	0.4	0.8	1.9	1.1	0.1
Biotite	0.1	0.3	0.1	0.1	0.2	0.1	0.2	0
Carbonates	0.2	0.2	3.7	5.9	36.8	21.7	13.9	13.3
Leather debris	0	0	0	2.5	1.1	0	0	0

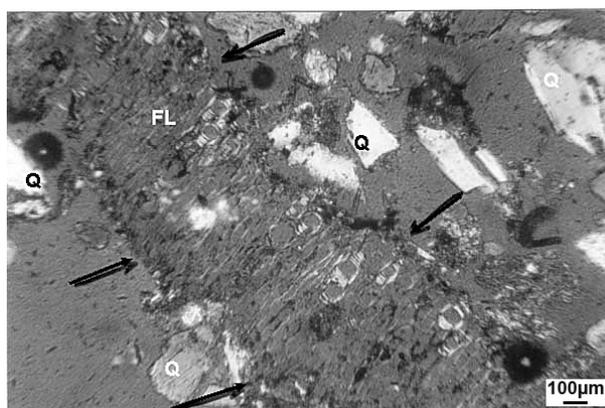


Fig. 4. Sediment from a canal draining the tannery waste water into the Dunajec River (site 1). Leather debris (FL – arrows) together with quartz (Q) are particularly abundant at this site. Thin section under optical microscope in partly polarized light. Magnification 60x.

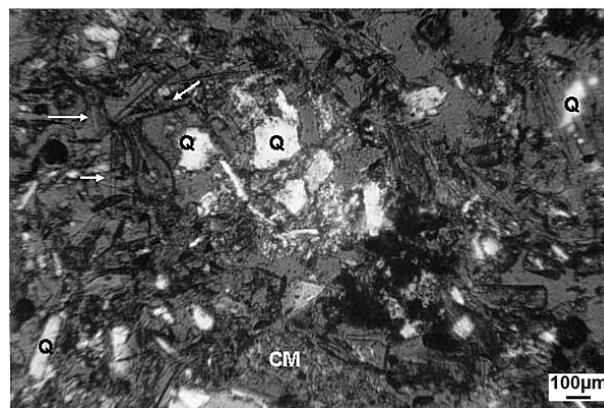


Fig. 5. Sediments from site 4, downstream from the Czorsztyn Reservoir, with fragments of diatom silica needles (arrows) between grains of quartz (Q) and mixed clay-organic background (CM) Thin section under optical microscope in partly polarized light. Magnification 60x.

rocks (site O and Ob). Note, however, the difference resulting from comparing the weight and volume percentage in sieving and microscopy, respectively. Sediments from site 2 show a considerably higher abundance of carbonates (Table 2). This is rather surprising and a local source for these carbonate-rich sediments must be postulated.

A mineral assemblage includes K-feldspars, plagioclase, muscovite and biotite, accompanied by fragments of sedimentary and crystalline rocks. Leather debris is relatively abundant in sediments from two sites close to the tannery discharges (sites 1 and 2). The sediment from the STP (sample 5) is composed of mostly a mixture of clay and organic matter with minor amounts of carbonate and quartz.

Anthropogenic Total Chromium in Sediments

Pseudo-total chromium concentrations (Fig. 7) in the BS (< 2000 µm) at sites located upstream of tanneries (Oc, Ob) and in the Białka River (O) are at the level of geochemical background (10–15 µg g⁻¹), while in the area close to the tanneries discharge they increase by two orders of magnitude (700–1600 µg g⁻¹). The enrichment factor is thus about 100. Downstream from the Czorsztyn Reservoir, Cr concentrations decrease significantly to 30–60 µg g⁻¹, but remain higher than those at the non-contaminated sites. Samples collected in both November and January show essentially the same trend. For comparison, the concentrations of Cr in the sludge from the STP (44

mg g⁻¹, site 5) and in a fragment of tanned pig skin (22.3 mg g⁻¹) were also determined.

Chromium Concentrations in Suspended Matter and in Different Grain-Size Fractions of Sediments

As the concentration of Cr can potentially be influenced by a preferential association of the metal with certain fractions [25], the concentration of Cr in the size frac-

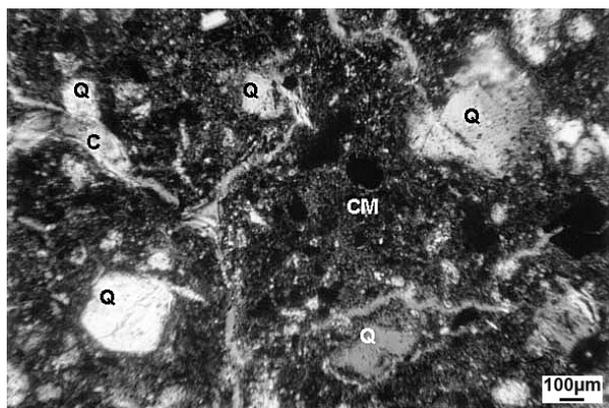


Fig. 6. Sediment from the sewage treatment plant STP (site 5). Dark-brown organic-rich clay matrix (CM) with organic detritus and detrital minerals, quartz (Q) and carbonates (C). Thin section under optical microscope in partly polarised light. Magnification 60x.

tions less than 20 μm has been compared (Figure 8). The concentrations in Figs. 7 and 8 show essentially the same trend, suggesting that the variation in the grain-size composition does not modify the contamination pattern.

At contaminated sites of the Dunajec River (sites 2 and 3), the concentration of Cr in suspended matter (22nd November 2003) is higher than Cr concentrations in various fractions of the SSL, while in the tannery discharge canal (site 1) it is slightly lower than in the organic fraction of the SSL (Fig. 9). At the non-contaminated site O, natural chromium is strongly enriched in the clay fraction (<2 μm), in contrast to the contaminated sediments (sites 2, 3), where the clay fraction is relatively poor in chromium. At the contaminated sites, chromium is more concentrated in the organic and coarse silt fractions (<2000 μm). A low concentration of Cr in the clay fraction is interesting, as it contradicts a common assumption that the concentration of metal contaminants increases with the decrease of particle grain-size. This may be due to a strong competition of organic matter for Cr in all size classes, precipitation of larger aggregates of chromium hydroxides and the presence of tanned leather debris at sites 2 and 3.

Similarly, no clear relationship between grain size and Cr concentration was found in the BS, samples of the polluted sites (1, 2, 3, 5) (Fig. 10). In contrast, Cr enrichment in the fine fraction (< 20 μm) is observed in the samples from the non-polluted Białka River, and decreasing Cr concentration with increasing grain-size is observed at site 4. Probably most of the sand-sized material settled

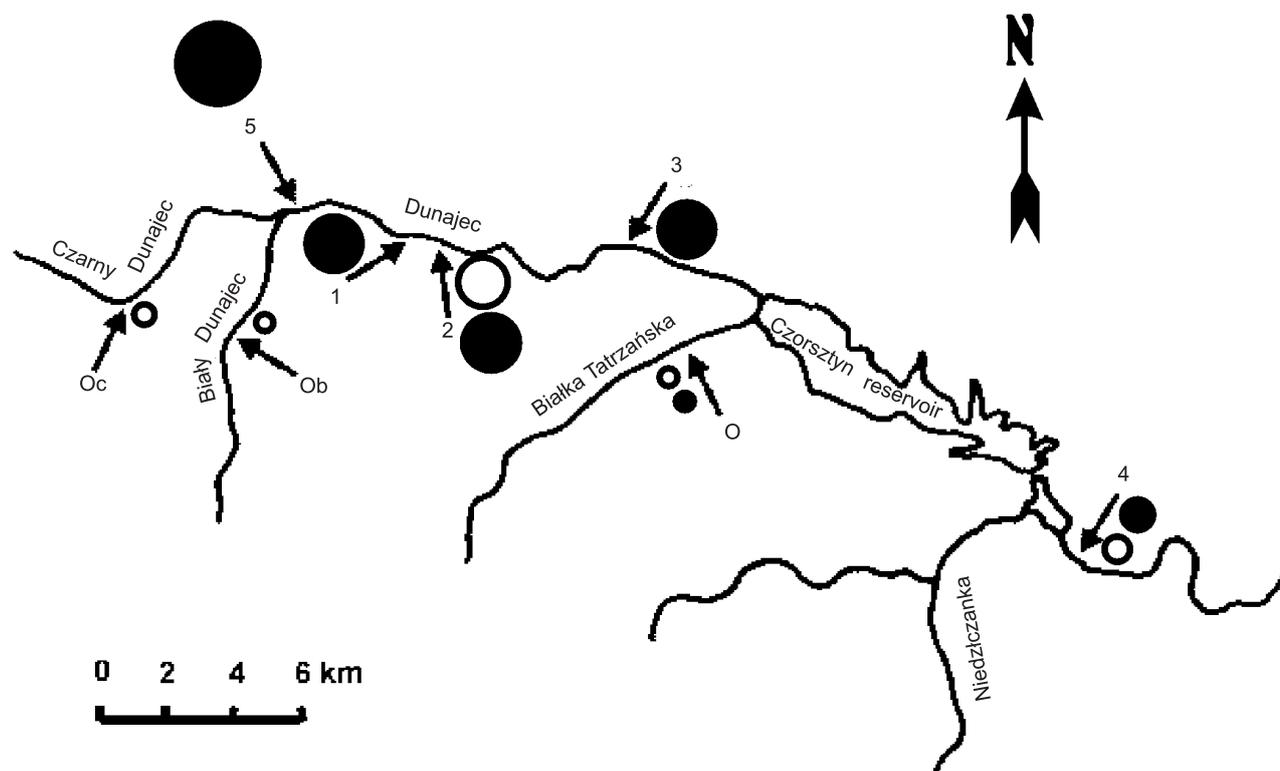


Fig. 7. Total chromium concentrations in the bottom sediments (BS, < 2000 μm) at the examined sites. Circle diameters are proportional to the logarithm of chromium concentration. Full circles – November 2003, open circles – January 2004.

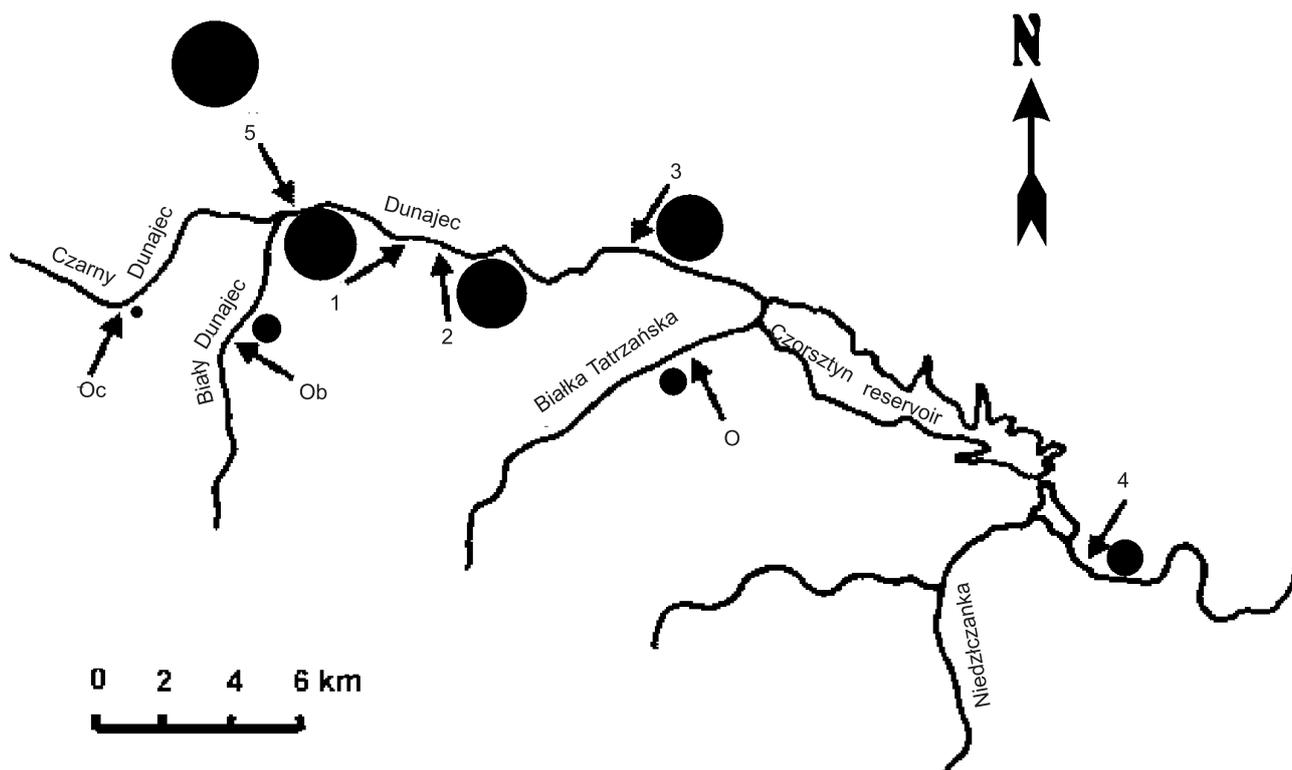


Fig. 8. Total chromium concentration in $< 20 \mu\text{m}$ size fraction of the bottom sediments (BS, November 2003) at the examined sites. Circle diameter is proportional to the logarithm of Cr concentration.

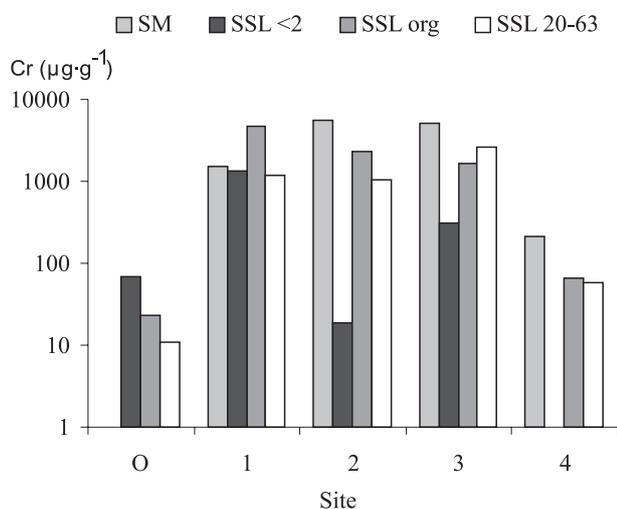


Fig. 9. Comparison of chromium concentrations in various fractions of the SSL and in the SM from sites O and 1-4. Missing bars at sites O and 4 are due to the concentrations below the detection limit. Size classes in μm . Note the logarithmic scale of chromium concentrations.

in the reservoir and sand fraction at this site originates from local sources with no, or little, Cr pollution from the upstream tanneries. At the polluted sites (1, 2), in same grain-size fraction (20-63 μm), chromium seems to be more enriched (up to factor 3) in the BS than in the SSL from the same site. This is not observed in the Białka River and in the Dunajec downstream from the reservoir.

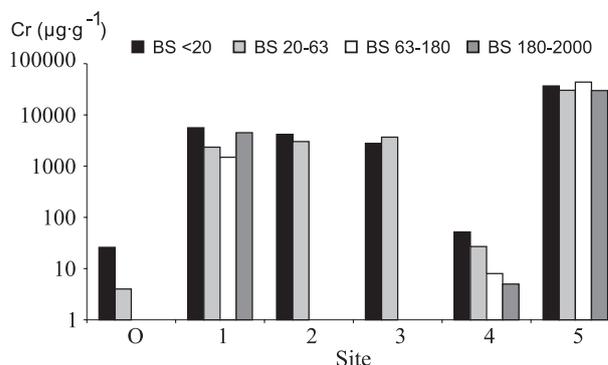


Fig. 10. Comparison of chromium concentrations in various size fractions of the BS from sites O and 1-5. At sites O, 2 and 3, chromium concentrations were measured in two size classes only. Size classes in μm . Note the logarithmic scale of chromium concentrations.

Although the age of the BS is not known, this observation suggests that the older sediments might be a potential source of contamination via erosion and resuspension.

No significant correlation was found between Mn or Fe and Cr in the sediments. Iron, (1 and 3% in the BS), is fairly homogeneously distributed between sites and between various grain-size fractions of BS, SSL and SM samples.

Manganese concentrations are quite variable ranging from less than 0.1 mg g^{-1} in the clay fraction of the Białka

River SSL (site O) to 58 mg g^{-1} in the fine fraction of the SSL sediment of site 4. In general, $<20 \mu\text{m}$ sediments from sites 2 and 4 seem to be enriched in Mn (up to 2.5 mg g^{-1}) than at other sites (0.3 and 0.7 mg g^{-1}).

This general variability of manganese in sediments is most probably related to the redox chemistry of this element which is soluble and mobile in oxygen depleted environments, whereas it precipitates as an oxide if sufficient oxygen is available.

The mineral composition of sediments reflects the petrography of the watershed rocks with the coarser, clastic grains composed of resistant minerals (quartz, K-feldspars, mica) derived from the granites of the Tatra Mountains and from the sandstones of the Magura flysch. The presence of fragments of carbonate rocks, more abundant in the Czarny Dunajec River and especially in the Dunajec River, mirrors the occurrence of calcareous rocks in the western Tatras (and possibly local sources in the Pieniny Mountains.). A higher content of clay and organic matter matrix at sites 2–4 reflects the increasing delivery of soil material eroded from cultivated fields and the input of sewage from urban agglomerations. This type of sediment has much larger sorption and retention capacity for metallic contaminants. The presence of leather fragments at sites 1 and 2 is due to the proximity of tannery effluent discharge sites. Leather debris have a high concentration of chromium. The pig leather specimen obtained from a local tannery contains 22.3 mg g^{-1} of Cr. A simple calculation shows that, with 1.2% of volume contributed by leather fragments in the sediment sample from site 1, the leather-bound chromium would not account for more than 10% of the total chromium content of this sample (1.46 mg g^{-1}), but it might contribute more substantially to the chromium content of the coarser fractions. Moreover, tiny leather debris, not distinguishable from the matrix under the optical microscope, can be responsible for a substantial part of the chromium contamination in the fine fractions. Fragmentation and microbial decomposition of the leather debris during transport result in the absence of discernible fragments at site 3, further away from tannery effluents. It is generally assumed that a large part of Cr(III) in sediments contaminated by tannery effluents is bound to organic matter or occurs as $\text{Cr}(\text{OH})_3$ and the results of extraction of Cr [3]. A recent study by Pereira de Abreu *et al.* [19] demonstrated a predominance of polynuclear hydroxy chromium complexes in water. This combined evidence and the enrichment of Cr in the organic fraction of the SSL may suggest that chromium in contaminated sediments occurs both as aggregates of polynuclear hydroxy complexes and undetermined Cr(III) forms bound to organic matter.

Cr concentrations in the SM at the contaminated sites are generally higher than in the individual fractions separated from the SSL. This is compatible with the timing of sampling coinciding with a high leather production period. Interestingly, the clay fraction in the SSL seems to be depleted in Cr while the slowly settling (organic) and coarse silt fractions have comparable concentrations

to each other. The inverse relation between grain-size and metal concentrations, usually observed in sediments, has not been found here. It suggests that a considerable proportion of chromium is delivered to the river from the tannery waste either bound to relatively large particles, or to a type of particles which may easily combine with large particles. Indeed, the chromium concentrations are similar in various grain-size fractions of sludge from the STP. Downstream from the reservoir, however, the usual pattern of the decreasing metal concentration with increasing grain-size is again observed, as larger Cr-contaminated particles settled in the reservoir.

Because of the lack of grain-size control at the polluted sites, the spatial distribution pattern of the total Cr concentration in sediments ($<2000 \mu\text{m}$) reflects the Cr sources and transport features: low, natural background concentrations upstream from tanneries, high concentrations close to the effluents from tanneries and a major decrease downstream from the reservoir. The latter observation points out to reservoir sediments as a major sink for chromium. This pattern has been previously identified [13, 16], but it is remarkable that the absolute concentrations in sediments at a given site in winter remain very similar three years later, although in summer they are distinctly lower, as contaminated sediments are flushed during spring floods. This indicates that sediment surveys can easily and conclusively be used to assess the implementation of waste management policy. As the Cr concentrations in water are variable due to intermittent input of wastewater, the sediment may be better suited for monitoring than occasional water surveys.

The Mn concentration in sediment shows relatively strong spatial variations. Sediments downstream from the reservoir are strongly enriched in manganese due to redox cycling of this element in the reservoir. There is no evidence of a relationship between Mn and Cr concentrations in sediments. This is of importance, as it has been suggested that manganese oxide may favour the oxidation of Cr(III) to Cr(VI) [26], enhancing Cr mobility and toxicity. The association of chromium, originating from tanneries, with Fe-Mn oxides in sediments was suggested [8]; however, neither Walsh and O'Halloran [3] nor Świetlik [27] found evidence of oxidation of Cr(III) to Cr(IV) in natural sediments.

The high level of Cr in sediments contaminated by tannery effluents might affect aquatic plants, zooplankton, benthic invertebrates and fish, and thus the biological compartments of the ecosystem need to be examined. Although generally accepted norms for an admissible level of metals in sediments do not exist, the concentrations of chromium above $1000 \mu\text{g g}^{-1}$ exceed the probable effect level (PEL) [28] of $90 \mu\text{g g}^{-1}$ by one order of magnitude. The PEL is considered as a threshold concentration above which adverse effects on aquatic life are usually observed.

The reported results on the toxicity of sediment-bound chromium are somewhat contradictory. A recent review of Rifkin *et al.* [29] suggests that no acute toxic-

ity of Cr in sediment is expected, as long as they are rich in acid volatile sulphides because only Cr(III) is likely to be present. Similarly, Besser *et al.* [30] found no decrease in survival of the amphipod *Hyalella azteca* in sediments spiked with Cr(III) up to 17 mg g⁻¹, although some effects on organism length and reproduction were observed. However, statistically significant acute toxic effects on *Hyalella azteca* were observed in some sediment from the Grand River (Michigan, USA) at a chromium concentration of 0.8 mg g⁻¹ [31]. At a comparable level of sediment contamination with chromium (mg g⁻¹), Leslie *et al.* [32] found clear adverse effect on benthic fauna in the Chusovaya River (Urals), such as reduced biodiversity and sublethal toxicity. Cooman *et al.* [33] found that tannery wastewaters were highly toxic to filter-feeders (*Daphnia spp.*). It should also be noted that genotoxicity of Cr(III) was observed in bacteria [34] and benthic invertebrates [35]. A high Cr concentration in vegetation and fish in a river contaminated by tannery wastes have been observed in Brazil [4]. These observations stress the need to study the impact of Dunajec River sediment contamination on benthic invertebrates, which are an important part of fish diet.

Results from Szalińska [16], confirmed in this study, indicate that the Czorsztyn Reservoir retains much of the chromium load and an intensive survey of the reservoir sediments is strongly recommended. Such a study carried out in White Lake, located near the eastern shore of Lake Michigan, revealed a strong contamination of surface sediment with Cr (2–4 mg g⁻¹). Although the direct discharge of tannery effluent to Tannery Bay in White Lake ceased in 1976, recent sediments are still contaminated, probably by resuspension of older, even more contaminated deposits [36]. These recent sediments appeared toxic for *Hyalella azteca* and to a lesser extent to *Chironomus tentans*, although no obvious relationship was found between total Cr concentration and toxicity. This shows the importance of chemical species and the association of metals with specific components of sediment in determining metal bioavailability and, consequently, toxicity [37].

Conclusions

Sediments of the upper Dunajec River, upstream from the Czorsztyn Reservoir, are severely polluted with chromium originated from tanneries. Chromium concentrations close to the natural geochemical background are observed in the sediments from the non-contaminated Czarny Dunajec, Biały Dunajec and Białka Rivers. Sediments from the Dunajec River close to tannery discharges show a high Cr concentration (4179 mg/kg), decreasing downstream of the Czorsztyn Reservoir, although it remains higher than the natural level. Thus, the reservoir serves as a major sink of chromium discharged from tanneries. There is no significant correlation between Cr and Mn, and between Cr and grain size in sediments and in

tannery sludge. The presence of leather fragments, observed under a microscope, confirms the direct input of tannery wastewater via small canals, without pre-treatment. Sediments can easily be used for the monitoring of discharge from tanneries and should be more extensively used for evaluation of wastewater management. Future research in the upper Dunajec should focus on the assessment of sediment toxicity to aquatic life.

Acknowledgements

We express our sincere thanks to the following colleagues: Mrs. Zofia Znachowska, Cracow University of Technology for carrying out the AAS analysis, and Mr. Tadeusz Podplomyk from STP in Nowy Targ for making available the sample of sludge. This work has been supported by the Polish KBN grant no 0539/PO4/2005/28 and Swiss NSF grant number 200020-101844.

References

- WARDAS M., BUDEK L., HELIOS-RYBICKA E. Variability of heavy metals content in bottom sediments of the Wilga River (Kraków area, Poland). *Applied Geochemistry*, **11**, 197, **1996**.
- MOLIK A., SIEPAK J., ŚWIETLIK R., DOJLIDO J. R. Identification of Chromium Species in Tanning Solutions. *Polish Journal of Environ. Stud.*, **13**, (3), pp. 311, **2004**.
- WALSH, A. R. AND O'HALLORAN, J. Chromium speciation in tannery effluent – II. Speciation in the effluent and in a receiving estuary. *Wat. Res.*, **30**, 2401, **1996**.
- JORDAO C. P., PEREIRA J. L., JHAM G. N. Chromium contamination in sediment, vegetation and fish caused by tanneries in the State of Minas Gerais, Brasil. *Sci. Total Environ.*, **207**, pp. 1, **1997**.
- ARMIENTA M.A., MORTON O., RODRIGUEZ R., CRUZ O., AGUAYO A., CENICEROS N. Chromium in a tannery wastewater irrigated area, León Valley, Mexico. *Bull. Environ. Contam. Toxicol.*, **66**, 189, **2001**.
- BARAKAT, S., GIUSTI L. Chromium speciation in a river system in Veneto (Italy) affected by tannery effluent. *Phys. IV France*, **107**, 115, **2003**.
- KOUKAL B., DOMINIK J., VIGNATI D., ARPAGAUS P., SANTIAGO S., OUDDANE B., BENAABIDATE, L. Assessment of water quality and toxicity of polluted Rivers Fez and Sebou in the region of Fez (Morocco). *Environmental Pollution*, **131**, 163, **2004**.
- KHWAJA A.R., SINGH R., TANDON S. Monitoring of Ganga water and sediments vis-à-vis tannery pollution at Kanpur (India): a case study. *Environmental Monitoring and Assessment*, **68**, 19, **2001**.
- LASEK W. *Kolagen. Chemia i wykorzystanie*, Wydawnictwa Naukowo-Techniczne, Warszawa, pp. 493, **1978**.
- MICHALEC T., Zakład Poligraficzny Wyższej Szkoły Inżynierskiej, Radom, pp. 446, **1996**.
- CHUAN M., C., LIU J.C. Release behaviour of chromium

- from tannery sludge. *Wat. Res.*, **30**, 932, **1996**.
12. KOTAŚ J., STASICKA Z. Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*, **107**, 263, **2000**.
 13. SZALIŃSKA E., DOMINIK J., BOBROWSKI A., BAS B. Fate of tannery chromium contamination in a stream: temporal and spatial evolution of chromium (III) and chromium (VI) *Journal of Physics IV*, **107**, 1275, **2003**.
 14. STYKA W., PŁAZA E., KABACIŃSKI M. Przebieg przemian biochemicznych w reaktorach SBR oraz efektywność oczyszczalni ścieków w Nowym Targu; in *Eksploracja i badania oczyszczalni ścieków SBR*, *Mat. Seminarium Naukowo-Technicznego*, Nowy Targ, pp. 39-53, **1998**.
 15. BANAŚ J., PŁAZA E., STYKA W., TRELA J. SBR technology used for advanced combined municipal and tannery wastewater treatment at high receiving water standards. *Wat. Sci. Tech.*, **40**, 451, **1999**.
 16. SZALIŃSKA E. Transformation of chromium in the water environment contaminated with tannery wastewater. *Monographs of Politechnika Krakowska (CUT)*, *Environmental Engineering issue*, **283**, 109, **2002**.
 17. DOMINIK J., BAS B., BOBROWSKI A., DWORAK T., KOUKAL B., NIEWIARA E., PEREIRA DE ABREU M.-H., ROSSÉ P., SZALIŃSKA E., VIGNATI D. Partitioning of chromium (VI) and chromium(III) between dissolved and colloidal forms in a stream and reservoir contaminated with tannery waste water. *Journal of Physics IV*, **107**, 385, **2003**.
 18. BOBROWSKI A., BAS B., DOMINIK J., NIEWIARA E., SZALIŃSKA E., VIGNATI D., ZARĘBSKI J. Chromium speciation study in polluted waters using catalytic adsorptive stripping voltammetry and tangential flow ultrafiltration. *Talanta*, **63**, 1003, **2004**.
 19. PEREIRA DE ABREU, M., H. DONARD, O.F.X., DOMINIK J. Speciation of chromium, using HPLC-ICP-MS, in surface water impacted by effluents from tanneries; in *10th Workshop on Progress in Analytical Methodologies in Trace Metal Speciation*, Luxembourg 6-9 April 2005, Abstracts, pp. 91-92, **2005**.
 20. PASTERNAK K. Charakterystyka podłoża zlewni rzeki Dunajec. *Acta Hydrobiol.*, **10**, 299, **1968**.
 21. BOGDANOWICZ E., CZARNECKA H., DOBRZYŃSKA I., FAL B., HOLDAWSKA I., JAROSIŃSKI W., MIERZWIŃSKI A., NASLAWSKA-MAJCHRZAK E., SZCZEPAŃSKI W. *Atlas posterunków wodowskazowych dla potrzeb Państwowego Monitoringu Środowiska*. Biblioteka Monitoringu Środowiska, pp. 312, **1995**.
 22. PUNZET J. Przepływy charakterystyczne; in *Dorzecze górnej Wisły*, Dynowska I., Maciejewski M. (eds.), Państwowe Wydawnictwo Naukowe, Warszawa – Kraków, pp. 167-215, **1991**.
 23. OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z. *Metody analizy i oceny właściwości gleb i roślin*. Katalog Instytut Ochrony Środowiska. Warszawa, pp. 333, **1991**.
 24. MROZIŃSKA-BRODA T., CZERWIK-MARCINKOWSKA J. Eucariotic algae and cyanobacteria in the River Dunajec upstream and downstream from the new dam reservoirs in Czorsztyn and Sromowce and their use for monitoring. *Oceanol. Hydrobiol. Stud.*, **33**, 83, **2004**.
 25. FÖRSTNER U., WITTMANT, G.T.W., *Metal pollution in the aquatic environment*, Springer, Berlin, pp. 486, **1979**.
 26. ŚWIETLIK R. Kinetic study of redox processes of chromium in natural river water. *Polish J. Environ. Studies*, **11**, 441, **2002**.
 27. RAID, EARY L-E., ZACHARA J.M. Environmental chemistry of chromium. *Sci. Tot. Environ.*, **86**, 15, **1989**.
 28. SMITH S. L., MACDONALD D. D., KEENLEYSIDE K. A., INGERSOLL C. G., FIELD L. J. A preliminary evaluation of sediment quality assessment values for freshwater sediments. *Great Lakes Res.*, **22**, 624, **1996**.
 29. RIFKIN E., GWINN P., BOUWER E. Chromium and sediment toxicity. *Environ. Sci. Technol.*, **38**, 267A, **2004**.
 30. BESSER J. M., BRUMBAUGH W., KEMBLE N., MAY, T. W., INGERSOLL C. G. Effects of sediment characteristics on the toxicity of chromium(III) and chromium(VI) to the amphipod *Hyalella azteca*. *Environ. Sci. Technol.*, **38**, 6210, **2004**.
 31. REDISKE R., BERTIN C., BLUNT J. QI M. Preliminary investigation of the extent of sediment contamination in the lower Grand River, US EPA 905-R-99-010, 156, **1999**.
 32. LESLIE H.A., PAVLUK T.I., BIJ DE VAATE A., KRAAK M.H.S. Triad assessment of the impact of chromium contamination on the benthic macroinvertebrates in the Chusovaya River (Urals, Russia). *Arch. Environ. Contam. Toxicol.*, **37**, 182, **1999**.
 33. COOMAN K., GAJARDO M., NIETO J., BORNHARDT G., VIDAL G. Tannery wastewater characterisation and toxicity on *Daphnia* spp. *Environ. Toxicol.*, **18**, 45, **2003**.
 34. PLAPER A., JENKO-BRINOVEC S., PREMZL A., KOS J., RASPOR P. Genotoxicity of trivalent chromium in bacterial cells. Possible effects on DNA topology. *Chem. Res. Toxicol.*, **15**, 943, **2002**.
 35. MICHAILOVA P., PETROVA N., SELLA G., BOVERO S., RAMELLA L., REGOLI F., ZELANO V. Genotoxic Effects of Chromium on Polytene Chromosomes of *Chironomus riparius* Meigen 1804 (Diptera, Chironomidae). *Caryologia*, **54**, 59, **2001**.
 36. REDISKE R., FAHNENSTIEL G., MEIER P., NALEPA T., SCHELSKE C. Preliminary investigation of the extent of sediment contamination in White Lake near the Whitehall leather tannery. Interagency agreement no DW13947766-01, U.S. Environmental Protection Agency, National Oceanic and Atmospheric Administration, 95, **1997**.
 37. BIELICKA A., BOJANOWSKA I., WIŚNIEWSKI A. Two Faces of Chromium – Pollutant and Bioelement. *Polish Jour. of Environ. Stud.*, **14**, (1), 5, **2005**.