Toxicity and geochemical analysis dredging Deep Water Navigation Canal Danube Black Sea

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Introduction

This report contains 7 chapters:
1. Geochemical speciation and toxicological effects of metals and organic micropollutants
2. Analysis of data
3. Conclusion on the data
4. Judgement of significance
5. Final Conclusion
6. Recommendations
7. Mitigating measures

Chapter 1 will give some background in geochemical speciation and toxicological arguments, to better understand the remainder of this report.

Chapter 2 will give an overview of the relevant information received and gathered from other sources to get an idea of the information necessary to judge on.

Chapter 3 will draw some conclusions from the data analysis.

Chapter 4 gives the arguments used to give the final conclusion to judge on.

Chapter 5 will give the final conclusion.

Chapter 6 gives recommendations for further investigation.

Chapter 7 gives some mitigating measures to avoid environmental problems.

1. Geochemical speciation and toxicological effects of metals and organic micropollutants

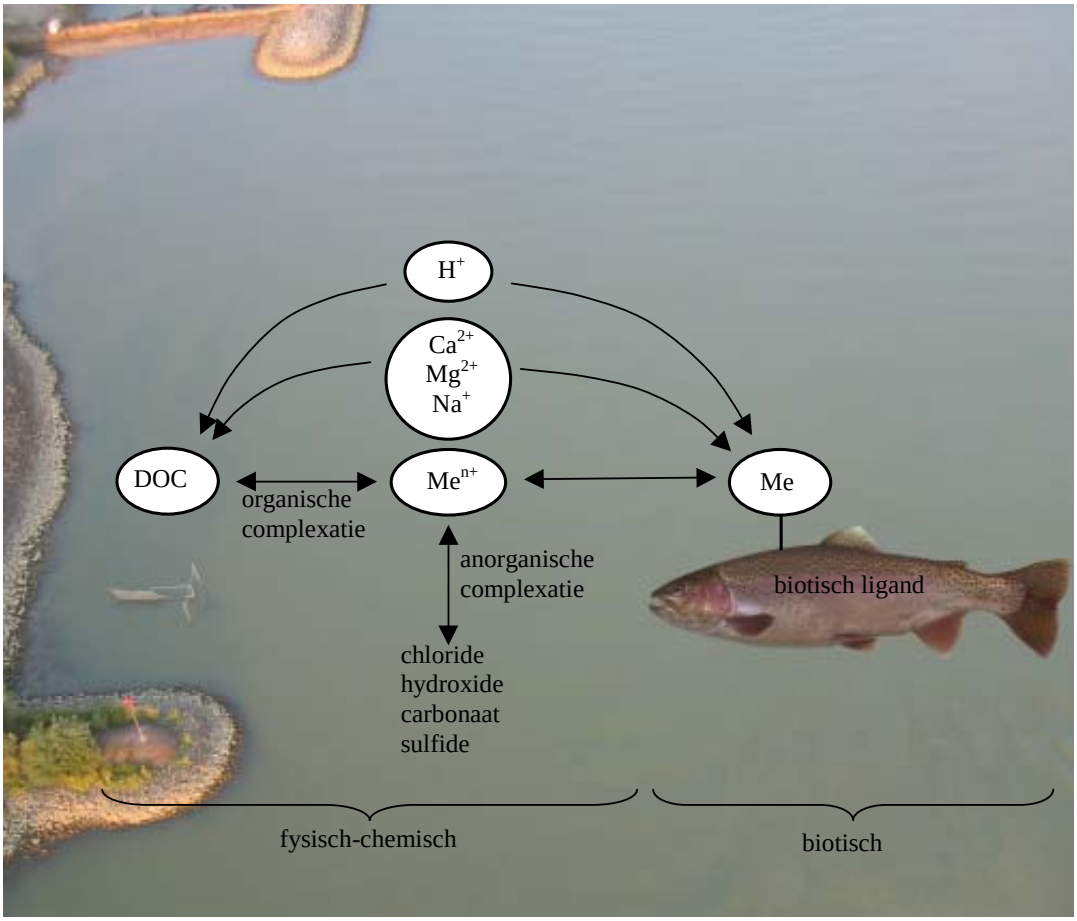
The toxicity of metals and organic micropollutants is caused by the adsorption or uptake of these compounds by living organisms in an amount, which disturbs the normal biochemical processes of these organisms. The effects can be mortality, less reproduction or anything else.
The amount of toxic component without any observed effect in chronic tests is called the No Effect Concentration (NOEC). Mostly a value is chosen as target value, which protects 95% of the relevant organisms.
In the natural environment, and especially the water environment, these compounds occur is several ways: dissolved and adsorbed to suspended matter. There are also a lot of dissolved species, e.g. in the case of copper: as Cu^{++}, $Cu(OH)^{+}$, $CuCl^{+}$, $CuHCO_3^{+}$, etc. The distribution of a chemical compound over different forms is called speciation.
In the past decades the normal way to derive standards for toxicity was to determine in a clean water system (without suspended solids or dissolved organic material) at what concentration of a toxic substance effects were observed in organisms (fytoplankton, fishes etc.) To derive standards for solids, the dissolved concentration was recalculated to a particular concentration with so called partition coefficients, which gives the relation between dissolved and particular concentration (on the assumption that there is an equilibrium between dissolved and particular concentration:

Concentration dissolved: Cd (mg/litre)
Concentration particular: Cp (mg/kg)
Partition coefficient: K = Cp/Cd (Litre/kg) or more often: (m^3/kg).

The partition coefficients are however very dependent on the chemistry of the system e.g. they can vary a tenfold with one pH unit. The amount adsorbed (or the concentration of absorbed material/litre of water (mg/litre) is dependent on the amount of suspended solids. But the concentration on the adsorbed material or the concentration of material/kg of suspended material (mg/kg) is not dependent on the amount of suspended solids. At the same chemical environment, the amount of adsorbed material will double when the amount of suspended solids double, at the same amount of dissolved material. For this reason there is a complicated recalculation scheme in the Dutch standards, where total concentrations are measured, to recalculate the measurement to a standard environment with 20 mg/litre of suspended solids. Thereby a general partition coefficient (although different for each compound) is used, which however neglects the fact that the partitioning coefficient is very dependent on the macrochemical environment. For organic materials this is especially the amount of suspended and dissolved organic matter, for metals this is the whole chemical environment, but especially the pH and the amount of dissolved organic matter. Finally, at higher pH's metals adsorb better than at low pH's.

According to the present scientific literature, we should not only exclude the adsorbed toxic materials (the particular fraction) as being toxic, but also several of the dissolved species. It is the common believe now that only part of all these several species is "seen" by an organism. The next figure gives an illustration of the speciation and the exposure to the organism (1). The organism "sees" the toxic metal, but also macrochemical substances like Ca^{++}, etc.

Not only the toxic metals can be bound to the bioligand, also other cations like Ca^{++}, H^{+}, etc. The cations also will adsorb to Dissolved Organic Carbon (DOC). This means that besides the amount of a toxic compound, also the total chemical speciation determines weather the occurrence of a toxic compound will have negative effects on the organism.



Conceptual framework of the bioligand modeling: the right part of the figure gives the organism (the bioligand) where a metal is bound.

In the framework of the Water Framework Directive (WFD) from the EU, Risk Assessment Reports (RAR) are now prepared to set the standards for toxic substances. (2,3,4)

This new approach seems to give higher values for toxicity levels for especially Zn and Cu, because these metals adsorb strongly to Dissolved Organic Carbon. The Dutch standard for dissolved copper and zinc should probably be a factor of 3 (or maybe more) higher than the present set value.
The same deviations in standards, because of adsorption to DOC also occurs for a lot of organic micropollutants (those who are hydrophobic, like PAH's and PCB's).
In this case it is a pity that we do not have data on DOC in the Danube. We do have dissolved organic nitrogen (personal communication Jos van Gils), which is in the order of .5 to 1 mg/litre. Taking .5 as the number and a conversion from nitrogen to carbon of 10 the DOC should be in the order of 5 mg/litre. The river Meuse and the river Rhine in the Netherlands are about 4 mg/litre, so they are probably comparable.

Since there is on this moment not a common set of standards within Europe, and there is a lot of scientific debate about the correct level of the standard, we will use the standards set by several countries or institutions to decide whether the measured concentration will probably be toxic or not.

Standards for dissolved concentration (Dutch);
Standards for total concentration (includes particular material) (Dutch, JDS, TNMN);
Standards for suspended and sediment concentration (Dutch and JDS);

Standards for mussels (JDS);
Standards for sediment dumping concentration (only Dutch);
Standards for dumping dredged material in salt water (only Dutch);

Table 1 gives an overview of the standards used.

In column 1 the pollutant is mentioned;
In column 2 the Dutch limit of dissolved concentrations is mentioned;
In column 3 the Dutch limit of total concentrations (dissolved plus suspended, recalculated to standard suspended material) is mentioned;
In column 4 the Dutch sediment standard is mentioned;
In column 5 the JDS limit of total concentrations is mentioned (it is not known if a recalculation to standard suspended solids has to be performed)
In Column 6 the ratio of standards between Dutch versus JDS is mentioned (for total concentrations in the water column). It is clear that the JDS standards have lower limits than the Dutch standards, Cu, Zn and Ni do not differ a lot, but the others differ more then tenfold.
In column 7 the JDS standards for mussels are given;
In column 8 the JDS standard for suspended solids and bottom sediments are given;
In column 9 the ratio of standards between Dutch versus JDS is mentioned (for sediment/suspended concentrations) are given. It is clear that the JDS standards have lower limits than the Dutch standards, but the difference are not so big as for the total water concentration.
In column 10, the Dutch standard is give for dumping dredged material without any permit or regulation (free dumping) of fresh water sediment into land or fresh water systems.
In column 11, the same application (dumping) as mentioned in the previous column is given but now for dumping sediment into the North Sea. Some of the standards are changed, because of the different geochemical behaviour in salt water systems: e.g. Cd has a lower limit, since Cd dissolves more in salt water because of complexation to chlorides.
In column 12 the TNMN for total water concentrations are given. (Target value Class II waters, table 4.5.1 (6))
In column 13 the ratio of standards between Dutch versus JNMN is mentioned (for total concentrations in the water column). For some metals the TNMN standards are more severe: (in diminishing order: Pb (44), Hg (12), As (6.4), Cd (2), Cr (1.68)) while others are less severe (in diminishing order: (Zn (0.4), Cu (0.19))

The difference in limits set by national institutes, or governments makes clear that is not easy or justified to look only at the numbers to decide whether a substance give ecotoxicological risk at a particular concentration or not.

In this respect it is good to mention that especially Cu and Zn (with less severe standards in the TNMN classification compared with the Dutch or JDS classification) show exceedance of Dutch limits (sometimes) and JDS limits (often). The metals Pb, Hg, As and Cr (with more severe limits in the TNMN classification) show seldom exceedance with the Dutch standards, or are far below.

Table 1

1	2	3	4	5	6	7	8	9	10	11	12	13
	Dissolved	Total	solid	JDS-total	Dutch total/ JDS total	JDS	JDS	Dutch total/ JDS total	Dumping	salt water dumping	TNMN	Dutch/TNMN
	Dutch	Dutch	Dutch	Joint Danube Survey					Dutch	Dutch	Trans National Monitoring networrk	
compartment	water	water	sediment	water	water	mussels	susp solids	sediment	sediment	sediment	Target value Total	
unit	microgr/liter	microgr/liter	mg/kg	microgr/liter	-	mg/kg	mg/kg	-	mg/kg	mg/kg	microgr/liter	-
cadmium	0.4	2	12	0.07	28.6	4	1.2	10.00	7.5	4	1	2
mercury	0.2	1.2	10			0.4	0.8	12.50	1.6	1.2	0.1	12
copper	1.5	3.8	73	3	1.3	20	60	1.22	90	60	20	0.19
nickel	5.1	8.3	44	1.8	4.6	10	50	0.88	45	45	50	0.166
lead	11	220	530	3.4	64.7	10	100	5.30	530	530	5	44
zinc	9.4	40	620	7	5.7	400	200	3.10	720	480	100	0.4
chromium	8.7	84	380	3.1	27.1	6	100	3.80	380	380	50	1.68
arsenic	25	32	55	1	32.0	20	20	2.75	55	55	5	6.4
DDT	0.4	0.9	0.009						0.04	0.02		
Sum-PAK's									10	10		
Sum-PCB's			0.004						0.2	0.2		
oil			1000						3000	1250		
lindane			0.23						0.02	0.02		
PCB28			0.004						0.03	0.03		

2. Analysis of data

We received a lot of information with measurement of toxic substances in de river system and the sediment. Often the information is confusing or even wrong. Sometimes the units are not mentioned, or the unit given must be wrong: e.g. in annex3.xls (**Water quality survey, 29 sept.2004 by Danube Delta National Institute)** values for suspended sediment for Zn are given in ppm (i.e. mg/kg) which are all below 1, or far below background levels.
There is also no clear indication what actual value we should use to determine the effects. There is a large range of concentrations in both time and space; both for dissolved in the water column as well as for suspended material. The variation in concentration in bottom sediments seems to be lower. According to the present regulation of the Water Framework Directive (WFD, European Union) judgement should not be done on one individual measurement or a maximum recorded value, but on yearly averages, or in some cases on the 90percentile value. For priority substances (e.g. Lead, Cadmium, PAH's) the yearly average value should be used, while for other substances (e.g. Zinc and Copper, the 90% value should be used.
To get the best possible insight also other sources of information were used. Very valuable information could be derived from the Joint Danube Survey report (5), and the Trans National Monitoring Network yearbook 2002 (6)

2.1 Metals

The data from annex3.xls (**Water quality survey, 29 sept.2004 by Danube Delta National Institute)** cannot be used (see above).

Annex4.xls (**Annex 4. Data from Transnational Monitoring Network)** data are given on macro chemical composition as well as total and dissolved metal concentrations in Vilkova (22 km) and Prut Reni (132 km) in the river, collected every month during 2004. The macro chemical composition can be compared to the composition of Rhine water (from which the Dutch standards are derived). For the averages of the metals Cr, Pb, Cd, Hg, and Ni, no exceedance above the Dutch standards is observed neither for dissolved, nor for total concentration, the maximum observed values do exceed the standards for Pb and Cd with about 50%. The averages of dissolved Zn and dissolved Cu, exceed the standard with 20% (Zn) and 300% (Cu). This holds for both Vilkova and Prut Reni. All values are above the JDS limits for total water concentrations

The Romanian national report for JDS:
Joint Danube Survey – Results for heavy metals – Romanian stretch
Data are given for water and sediment samples of the JDS stations 94 (Prut (135 km), 95 (Reni (132 km)) and 96 (Vilkova (18 km)) In the water samples, the maximum Zn concentration exceeds the Dutch limits 3 fold, Cu two fold. All water samples exceed the JDS standards (Zn tenfold, Cu 2 fold, Cd 30 fold, Pb two fold and Ni twofold), only Cr is below the JDS standards

In the sediment samples, only Cu exceeds the Dutch limits 3 fold. The JDS limits are exceeded for all metals.

Results of water quality monitoring.xls (Ukraine (8 march)) gives a compilation of the measurements at Reni (132 km) and Vilkova (18 km) of the year 2001 is given. The flow measurements are daily, the quality measurements are twice/month or monthly, except the dissolved metals, which were done only twice. At both Reni and Vilkova total Cu exceeds the Dutch standard twofold. All metals exceed the JDS standard.

Annex20 (chemical testing results for bottom sediment samples (25-28 May 2004):
Results are given for the sediment composition in the Chilia Branch and the Bystre branch and for 11 Riffle's (from 24 till 74 km) as well as three locations in the outer delta. The metals Hg, Cd, Pb, Cu and Zn are measured. Measured are also oil products.

Except for Cu at one riffle, (1.16 above the standard) all measurement are below the Dutch standard for sediments, Except for two Riffle's (with exceedance for Cu and Zn) they are also all below the JDS standards for suspended solids.

The JDS report contains graphs of metals along the Danube river:
In annex a the total and dissolved concentrations in the water column
In annex b the suspended matter concentrations
In annex c the sediment concentrations
In annex d contains some depth profiles in the sediment
In annex e concentrations in Mussels

In the next table the result for the lower 250-km stretch is compiled, together with some standards, the number gives the highest value; bold are measurement above a standard. Bold an italic above both (JDS and Dutch) standards

metal	Suspended maximum	Sediment maximum	Mussels maximum	JDS stand Sediment	Dutch stand sediment	JDS stand Mussels
Unit	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Cd	**2**	**2**	**10**	1.2	12	4
Cr	100	100	5	100	380	6
Cu	**70**	***100***	**60**	60	73	20
Hg	0.4	0.7	.2	0.8	10	0.4
Ni	***80***	***70***	3	50	44	10
Pb	50	80	10	100	530	10
Zn	200	200	**600**	200	720	400

From this data it appears that there are 4 problematic metals, Cd, Cu, Ni and Zn. Note however that the sediment concentrations hardly differ from the suspended matter concentration and that the exceedance of the standards, except for Cd and Cu in mussels is rather small.
The depth profiles (only between JDS 20 and JDS 63) do not show great variation with depth, only for Pb which seem to be lower near to the surface. The graphs for Cu en Ni (suspended and sediment) are given in the appendices of this report.

Impact assessment Ukraine 8-nov 2004
In table 4.3.5 data are given on the total concentration of some heavy metals in de water column, for the Kiliya delta and the Bystryy arm. Cu and Zn are above the limits; Pb and Cr are below.
In table 4.3.7 and 4.3.8 metal concentrations of the bottom sediments in the Danube (section Oily-Rein. 182-32 km) and in the sediments of the delta and seaside of the Danube are given. Cu exceeds the sediment limits (maximum up to 110 mg/kg) as well as Ni (maximum up to 62 mg/kg). This seem to be individual measurements
The average concentrations in the delta and the seaside are about 50 mg/kg for Cu, with maxima up to 200. For Ni the average is about 60, with maxima up to 400, while Cd is 6 mg/kg with maxima up to 17 mg/kg.
Table 4.3.14 gives average content on bottom sediments for metals, oil products and DDT. All values for the metals are below the Dutch standard for sediment, Zn and Pb, are slightly above the JDS limit for suspended solids (less than 1.1), Cu and Cd exceed the limit by more than a factor of 2.

Annex33 (Ukr)
Annex33 gives average content in bottom sediments (we assumed that the unit of mck/g is mistyped and that micrograms/gram or mg/kg have to be used). In this document the average content in bottom sediments is given for 5 metals. They all exceeds the JDS standard for suspended solids, only Cu exceeds the Dutch standard for sediments, (almost twofold).

Annex37 (Ukr)

Table 1 in annex37 gives the sediment composition in the stations S1-S16 (I did assume that these are the stations given in a figure annex_6c.doc: “The observational posts for monitoring in the river”.)
Pb and Zn are below the sediment standards, Cu exceeds the standard in only one measurement (12%), Ni in 3 measurements (maximal 26%), and Cd in most samples, maximum is 2.7 mg/kg, with a JDS standard of 1.2 and a Dutch standard of 12 (mg/kg).
Table 2 gives the result of a filed survey on Molluscs from 25-10-2004. None of the metals exceeds the standards.
On page 8 the results of field surveys in 2005 on bottom sediments are given: only Cd seems to exceed the JDS sediment standard (maximum value is 3 mg/kg)
Table 7 gives the result of a field survey in August 2005 for heavy metals in mollusc Tissues.
None of the measurements exceeds the JDS limits for molluscs, however they exceed the limits for non-prey fish.

2.2 Organic micropollutants

In the Romanian national report for JDS
PAHs concentration levels in Danube sediment samples - Romanian sector
Data are given for PAH’s (the 16-EPA), PCB (the standard 7), HCH, all in sediment and HCH in water, for the JDS station 94, 95, 96.
All PAH’s are given mostly as not detectable or 0.000 (mg/kg), a few 0.001 values occur, one 0.009 for fluorene at JDS 96. This implies that all values are far below the standards
PCB’s are recorded mostly as not detectable or 0.000 (mg/kg) except PCB-52 at JDS 96, which is 0.002 (mg/kg) (with a standard of 0.004)
G-HCH (lindane) is below the standards in both water and sediment compartment.

In annex20 (chemical testing results for bottom sediment samples (25-28 May 2004)
Also oil product are measured. The numbers are all below 350 mg/kg while the sediment standard is 1000 mg/kg

The JDS report contains data of PAH’s along the Danube river:
Phenanthrene and Antracene dominated the PAHs contamination in most of the sediment samples; however, the sum of the PAHs rarely reached the 2 mg/kg, which is below the standards.

3.0 Conclusions from the data

There is a lot of scatter in the data and some useful information is missing, which makes it difficult to draw conclusions.
What is missing:

- Depth profiles at the location of dredging (is there old contaminated sediment??)
- Measurements of DOC in the water column.
- Measurements of the macrochemical composition of the sediment ($CaCO_3$, Iron oxides, sulphide organic material content etc.)
- There is a lot of information on the concentration of toxic materials in the suspended solids, but given as mg/litre (or microgram/litre). Without the accompanying measurement of the suspended solids concentration itself, these measurements are useless for judging toxicity.

Metals

However from the above given compilation of data it appears the metals of concern are Cu and Zn and sometimes Cd. There also seems to be hardly difference in metal concentrations in suspended material (within the water column) and the concentrations in the bottom sediments, except maybe for Cu (above the standard) and Pb (below the standard).
It also look like that the standards in the water column (dissolved concentrations) are much more violated than the standards in the sediment (solid concentrations).

Organic micropollutants

From the available data it cannot be concluded that PAH's, PCB's, lindane, or oil products are above the standards in such a way that they can cause problems..

4.0 Judgement on significance

Dredging activities always result in a spill on the dredging location. Thereby sediment material comes into the water column and often in a different chemical environment. The same processes take place at the dumping site, which in this case is macrochemical much more different (sea water). Especially oxygen plays a key-role in this process. The porewater is mostly within a few centimetres depth in the sediment without oxygen. Sulphate and iron reduction and methanogenesis then determine the chemical environment. Most heavy metals will be bound as very insoluble sulphides. When this material (solid plus porewater) is brought to the water column oxidation processes prevail. Thereby the oxygen concentrations in the water column may drop. These oxygen-effects may be harmful to organisms, however it is the Dutch experience that fishes just will swim away to locations where there is enough oxygen. Since often the dissolved concentrations of N and P in the porewaters are much higher than in de surface water (because of the decay of organic material in the sediment) an increase in N and P is also often observed. These effects are normally locally and for a short period (order of maximal days). What happens with heavy metals when high concentrations of suspended material occur due to the load of bottom sediments? In Dutch dredging operations it was concluded that the total concentration did go up, but that the dissolved concentration did seldom go up or even did drop. (7) One reason is the oxidation of FeS to iron oxides with the subsequent adsorption of heavy metals to this freshly precipitated FeOOH, which has a high surface (small particles) and subsequent a high adsorption capacity. Another reason is the difference in pH between sediment porewater and overlying water. The porewater of the sediment (under the assumption of relative organic rich sediment, and an alkalinity in the overlying water of at least 2 mmol/litre) is often .5 till 1.0 pH unit lower. When sediment in equilibrium with this pH is brought to the overlying water with a higher pH it gets a higher adsorption capacity for metals. So the increase in total adsorption capacity and the higher affinity for metals may cause a decrease in dissolved concentration.

The proper way to make a prediction is to use numbers on sediment losses (as is done in annex 33 (UKR)) in a geochemical speciation model, which calculates the geochemical species in the water column, which in combination with a bioligand model calculates the measure of toxicity. Jos van Gils has estimated sediment losses during dredging and dumping, including the southwards plume formation in the Black Sea. Geochemical modelling however requires more accurate data than presently available, so we will confine ourselves to an estimate. From the above pictured geochemical processes which take place during dredging and dumping, it is clear that in any case the increase in toxic appearances of substances is much smaller than the increase in suspended matter (on a percentual base).

Increasing the suspended solids concentration may have negative effects on all kind of processes and organisms. However if the added amount of sediment has the same concentration of toxic material (in mg/kg solid) and the same binding capacity (which depends on the macro chemistry of the water and the properties of the added sediment in relation to the original suspended material) as the original amount of suspended sediment, **nothing will happen** with the dissolved concentration and with the concentration which the organisms “see” with respect to toxicity.

In the Ukrainian environmental impact assessment an approach is given to estimate the effect of dredging and dumping on total water quality. This approach assumes an amount of solids to be lost into the water column and calculates the increase in total concentration in the water column, dependent on the flow rate. Then it calculates the percentile increase in total water concentration of metals because of the spill of dredging. This method assumes that all “lost” sediments will expose their contaminants to the water column and the organisms. This is a worst case assumption and can be refined.

The pH in the Black Sea is probably above 8, since the “natural” pH for hardwater salt water systems is about 8.3. The Danube is a hard water river, and the water below the halocline in the Black Sea is reducing sulphate, thereby producing alkalinity, which is an extra effect to result in higher pH’s. At higher pH’s all heavy metals are more in the adsorbed phase than in the dissolved phase, which reduces the toxicological effects of these metals.

5.0 Final Conclusion

Especially Zn and Cu are the metals which exceed the standards most, metals for which has been shown in recent years that they need refinement in the way the standards are derived (the DOC effect). So is not sure if these metals are really present in toxic quantities

The amounts of sediment contamination are all well below the Dutch standards for dumping (fresh water) sediments into the North Sea. So, according to the Dutch standards there will be no toxic effects.

But even if there are at present toxic effects it is unlikely that because of the dredging and dumping of dredged material these effects will increase, since the dredged material has more or less the same composition as the bottom sediment.

So finally:
Based on the available data: is impossible to conclude that a significant impact with regard to toxicological effects will occur neither at the dredging site, nor at the dumping site.
Based on the available data it is unlikely that significant effects will occur

6.0 Recommendations

The present available data sets about sediment quality do not contain any indications about the depth within the sediment where the samples were taken. Probably it are all surface samples. Since dredging may occur till a depth of about 3 meters, samples should be taken over the whole depth profile, to find out if maybe older (more polluted) sediment is present. The locations of these samples should be determined in such a way that a representative image is obtained of all the material to be dredged.
In those samples not only the pollutants (mg/kg) should be determined, but also the macrochemical composition.

- Grain size (<2μ, <16μ, etc)
- $CaCO_3$ content
- Fe content
- Sulphide content
- Organic material content (percentage organic C)

Without these macrochemical measurements it is difficult to judge the toxic effects of micropollutants.

It is also advisable to measure the same parameters in the suspended solids.
N.B. not measure pollutants in mg/litre of water but in mg/kg of solid!!

Finally one should measure the Dissolved Organic Carbon (DOC) in the watercolumn

7.0 Mitigating measures

Spreading of sediment, during dredging, or dumping of dredged material, even if it is not toxic, may be harmful to the environment (covering fish eggs etc.)

During dredging, spreading of sediment can be contained to the dredging location itself, by putting curtains from top of the watercolumn till the water/sediment interface around the dredging location.

If the dredged material is not dumped by opening the floor of the boat (which is the easiest way) but by reloading it with a grab-bucket, or by pumping equipment into a large tube which has its end just above the sediment surface of the dumping location, spreading of sediment material will also be prevented.

Finally, if higher heavy metal contents are found (in the deeper sediment) than till yet reported, it might be an option to dump this material below the permanent halocline in deeper water. This water is very rich in sulphides and will thereby bind all heavy metals permanently into metal-sulphides.

Literature

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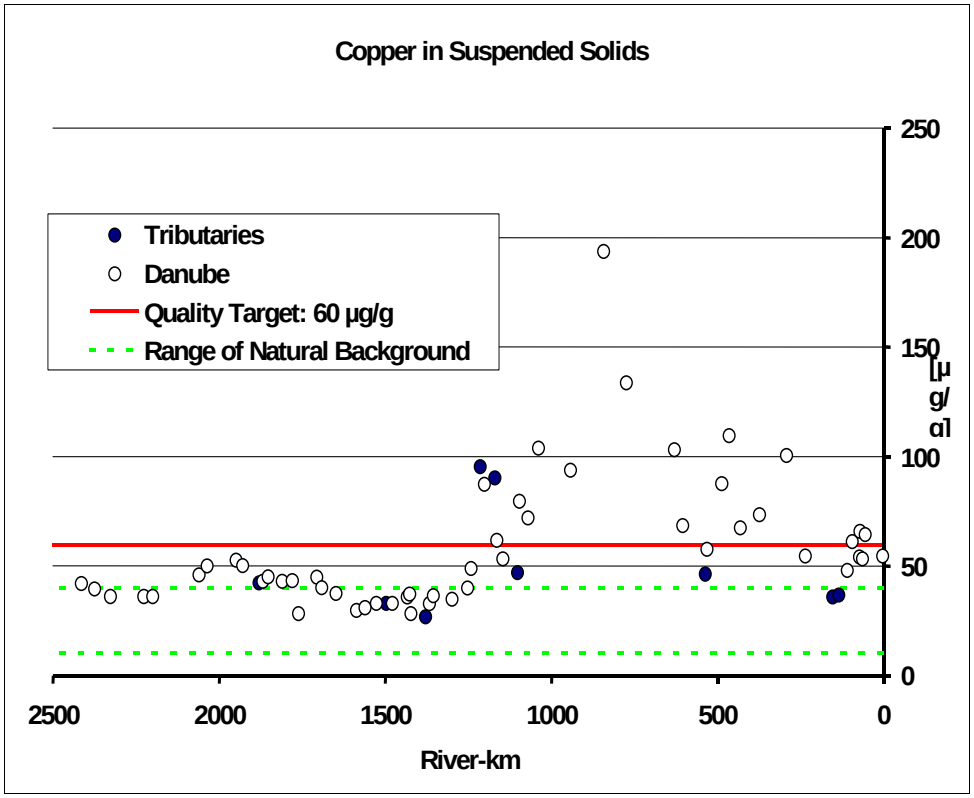
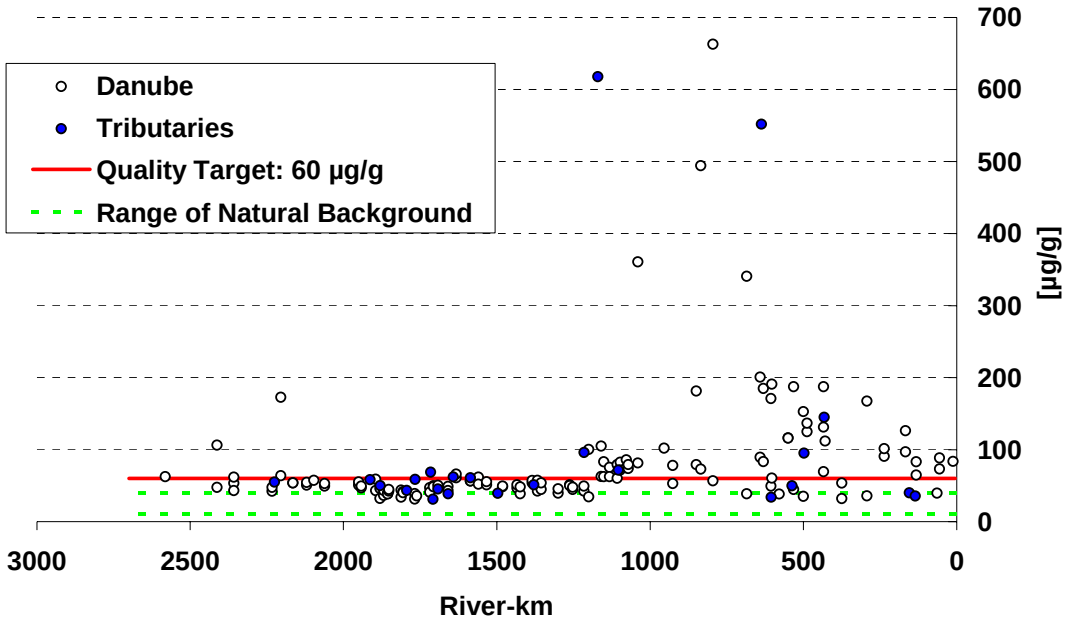
Copper in suspended solids and sediment, JDS survey



Copper in Sediments



Nickel in suspended solids and sediment, JDS survey