INORGANIC POLLUTANTS OF THE SYR-DARIA RIVER (KAZAKH PRIARALIE)

Gadalia Alain, Motelica-Heino Mikael, Serra Hélène,
Abou Akar Afif, Jouin Frédéric, Charpy Antoine
Bureau de Recherches Géologiques et Minières, 3, Avenue Claude Guillemin, BP6009,
45060 Orléans Cedex2, France

Detailed Summary

Within the framework of the INTAS program on the Aral Sea Basin, the "Aral 1072 project", a state of the water quality of the Syrdarya River was implemented during two field campaigns in September 2003 (low water period) and April 2004 (high water period) in the Kazakh Priaralie (Syrdarya valley in Kazakhstan). This paper presents the study of the dissolved inorganic species from key sampling places in the river. Attention was paid to the methodology of sampling by following international recommendations in handling, preservation of the samples, in physical-chemical measurements on site, in low level trace analytical methods and in an appraisal of the uncertainties from the field to the laboratory (duplicated samples, field blanks).

In agreement with the available former data the decrease of the Heavy Metals contents was confirmed. Although the aridisation, including a salinisation of the soils and of the precipitations is well established in the region (and particularly near the Aral Sea), no increase of the salinity was clearly demonstrated for the river neither for the last decade and for the Kazakh Priaralie. Nevertheless the salt content (TDS and SO_4) was the only parameter that does not comply constantly in some places with the local or European standards of water quality.

The current Syrdarya River water quality is influenced by several phenomena:

- most of major dissolved species (TDS) are mainly controlled by dilution and thus by the river flow rate that depends itself on the season and on the Chardara dam regulation.
- lakes of the delta zone may contribute to an increase of the salinity of the river on the flooding period when they are connected to it
- many heavy metals (Ni, Ti, Sn, Cu, Co,…) come from the leaching of upstream mining areas or agricultural wastes during the snow melting at spring
- the salt content (TDS), nitrates, silica and some heavy metals decreased in September 2003 in the Chardara reservoir because of phytoplankton absorption
- carbonate precipitation due to higher temperatures is also inferred in September in the Chardara reservoir
- various discharges contribute to the pollution of the river. Besides agricultural fertilizers (NO_3 at spring), the urban waste waters (bringing Suspended Particulate Materials, Dissolved Organic Carbon, lowering the oxygen content of the water,…) and some industrial (present or passed, local or upstream) activities may impact the river
- the geochemical regional background influences the composition of the river (Sr abnormal concentrations)

Introduction

Considering the Aral Sea environmental disaster, the Syrdarya River played a role both of a target and a vector. Just like the Aral Sea into which it flows, it suffered from the huge withdrawal of water resulting of the former intensive irrigation system. Its flow rate decreased from 43.3 km^3 during the 60's to 2 km^3 per year in the first half of the 80's (Lŭtolle and Mainguet, 1993). Along with the drop of the river flow rate, the aridisation of the climate, the soils degradation including their salinisation, the mineralization of the surface and shallow ground waters were strengthened. At the same time its waters transported dissolved and suspended pollutants that presumably ended in the Aral Lake. Those pollutants resulted mainly from the agricultural drainage canals net bringing fertilizers and pesticides on one side, from waste or run off waters, discharges from mining, industrial and/or urban centers all the river course along on the other side.

New projects of remediation in the Northern Aral Sea (Kok-Aral dam completed in August 2005) and in the Syrdarya valley (to double the river flow rate by heavy civil works) are coming. A common transboundary management of the whole Aral Basin water resources is in question between the 5 new independent states. Signs of starting up again appeared after the 2000's in the economy of Kazakhstan. This new situation justifies the implementation of an assessment of the river water quality.

This paper is a contribution to this purpose. It results from a European Union – BRGM co-funded project within the frame of INTAS, the "Aral 1072 project".

Materials and Methods

We will mainly consider here, among the dissolved inorganic species of the Syrdarya River,

- the heavy metals and other trace elements
- the major chemical species that can result from the salinisation process (sulphates, sodium, chlorides, magnesium,…) and from fertilizers (nitrates)

The Kazakh Priaralie, i.e. the Kazakh part of the Syrdarya Basin starts upstream the Chardara reservoir (the Uzbek border) till the present sea shore of the Small Aral Sea, about 1500 km downstream.

Syrdarya River has one high water season (snow melting from April to May) and a low water one (from September to February).

Our analytical data result from two sampling campaigns: one at the low water period in September 2003 and a second one at the high water period in April 2004 (table 1a, 2a).

ISO 5667 recommendations were followed as much as possible during our sampling programme.

Sampling places were selected up and downstream 6 key-places supposed to play a role either in the contamination or in its attenuation: (1) the Chardara reservoir, (2) the confluence with Arys-Turkistan canal and Arys river, a right bank tributary crossing the industrial city of Chimkent, the cities of (3) Chi-Ili, (4) Kyzyl-Orda , (5) Jalagash and their respective irrigated areas, (6) the delta zone (and still some irrigated areas)

River waters were collected in the middle of the channel or at least in the main stream. In September 2003 two levels of the river water column were sampled: at 1m below the surface and 1m above the bottom. During the second mission all the samples were collected at one meter depth (table 1b).

Water samples were filtered under nitrogen pressure with 0.45 µm cellulose acetate filter. Filtrate samples were dispatched into 3 bottles: (1) one acidified to pH ≤ 2 with ultra-pure HNO_3 for the cations and trace elements analysis, (2) another one filled up to the top for the anions and (3) the last one acidified to pH ≤ 2 with ultra-pure H_2SO_4 for the Dissolved Organic Carbon (DOC). Filters had been weighed before and after the campaigns to quantify the Suspended Particulate Materials (SPM) content.

During the September 2003 campaign, all the samples were systematically duplicated and field blanks collected.

Specific Conductance, temperature, dissolved oxygen, redox potential and pH were determined on site.

Alkalinity was determined on filtered samples by the Gran method.

Transportation times exceed the recommended time limits for NO_3, and at a lesser extent for SO_4 and DOC. A few analytical controls (alkalinity measured on site and calculation of the ionic balance) did not show significant impacts on the results.

Laboratory analyses

The determination methods and the Lower Levels of Quantification of the BRGM laboratory comply with the standards of the COFRAC certification for the analyses of major species in the waters. The cations and silicium were analysed by emission ICP, Cl^-, SO_4^{-2} and NO_3^- by HPLC (Dionex), HCO_3^- by potentiometry and DOC by persulfate oxidation under heat.

A high performance ICP/MS (Thermo Plasma- Quad 3 model) analysed trace elements (table 1b and 2b). For each element and at each series of analyses Lower Levels of Detection and of Quantification were calculated. The Lower Levels of Quantification ranged from 1,2 for Fe till 0,01 µg/l for Mn, Rb Tl in both campaigns.

Appraisal of uncertainties

In several samples of both campaigns, some trace elements (B, Al, Fe, Zn, Pb, Mn, Cu, Cr, Sr,…) were detected in the field blanks at higher concentrations (and significantly higher than the determination threshold) than in the corresponding samples. We cannot preclude a contamination coming from the equipment although the width of the spectrum and the nature of the contaminating elements suggest that their origin are not (only) processed materials but natural source and namely an atmospheric origin. Savenko and Kulmatov (1997) already mentioned the curious anomaly of Zn concentration in the soils of the Aral Sea Basin. They suggested a link with the precipitation composition that is abnormally high for Zn in the region.

The standard deviations were calculated in order to estimate the relative uncertainties. Some elements (Al, Cr, Fe, Cd, Zn) presented a higher uncertainty due to the ICP/MS method and some more intricate matrices.

Table 1a . Results of the on site measurements - September 2003.

N° sample	Depth	Sampling time	Sampling place	GPS coordinates .			Water Temp	Elec.Cond.25°C	Diss. Oxy-gen	Redox Pot.	PH	Alka-linity	Equivalent TIC
				Longitude	Latitude	Altit.	(єc)	uS/cm	mg/l	mV		meq/l	mg/l
SD1	1m	12/09; 18:00	Bridge upstream Chardara reservoir	68° 31'08 E	41°01'78N		23.7	1855	9.67	474	7.8	3.94	47.3
	3,5m	12/09; 19:00					23.4	1873	10.31	433	7.8	3.97	47.6
SD2	1m	13/09; 12:30	Karasakal village, upstream and south, bank of Chardara reservoir	68° 08'18 E	41 ° 03'30 N		21.7	1969	9.21	415	7.8	1.76	21.1
SD3	1m	13/09; 19:30	Zolotye Pesky, 7 km before Chardara dam, south. Bank	67° 55'48 E	41° 12'19 N		22.5	1472	9.08	480	7.5	2.31	27.7
	2,5m	13/09; 19:45	Idem				20.9	1426	9.68	456	7.5	2.24	26.9
SD5	1m	14/09; 12:45	Chardara city downstream from the dam, right bank	67° 57'39 E	41°15'05N		24.4	1569		433	7	2.44	29.3
	2,5m	14/09; 13:00	Idem				23.9	1554	6.01	406	6.6	2.38	28.6
SD6	1,3 m	15/09; 9:00	60 Km upstream from the con-fluence of the Arys river, right bank	68° 15' 04 E	42° 18'11 N		19.1	1674	9.2	453	6.9	3.08	37.0
SD8	1,5m	16/09; 12:30	Near Aqkol hamlet	67°51' 04 E	43° 09' 37 N	168m	22.5	1507	17.05	380	7.02	2.22	26.6
SD9	1m	16/09; 19:00	Downstream from Chi-lli	66° 22'13 E	44° 16' 31 N	138m	25.1	1557		369	6.24	2.25	27.0
	5m	16/09;19:30	Idem				23	1630		211	6.02	2.42	29.0
SD10	1m	18/09; 9:00	Downstream from Kyzyl-Orda	65° 17' 4E	44° 59' 1 N	111m	17.2		0.78	351	7.75	2.5	30.0
	4,5m	18/09; 9:30	Idem				16.4			419	7.04	2.38	28.6
SD13	4m	19/09; 8:30	Jalagash bridge	64° 33' 05" E	45° 02'49" N	105m	16.9		0.89	425	7	2.46	29.5
SD14	5,5m	21/09; 12:00	Karateren bridge	61 ° 02'22" E	46° 02'14" N		17.8		9.34	433	6.73	2.71	32.5

Table 1b. Average values of the chemical analyses on duplicated water samples from the Syrdarya River.

n° sample	SPM	TDS	DOC	IB	Ca	Mg	Na	K	HCO_3	Cl	NO_3	SO_4	SiO_2	B	Al	Ti	Cr	Fe	Mn
	mg/l	mg/l	mg/l	%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
SD1-1m	263	1456,7	2,2	-0,6	143,2	79,6	156,6	4,8	245,4	100,8	9,1	700,5	13,3	334	7,0	7,4	1,2	14,3	9,1
SD1-3.5m		1485,6	2,4	-1,3	147,7	79,4	156,1	4,8	249,4	102,0	10,0	719,5	13,2	358	10,9	10,7	1,6	25,2	11,6
SD2-1m	56	1446,0	5,4	-0,9	116,3	70,0	205,1	5,4	128,5	127,0	<0,1	775,5	14,2	419	13,2	13,0	0,5	21,6	12,1
SD3-1m		1080,1	3,4	-0,5	94,5	62,9	124,6	4,5	144,5	81,5	0,6	551,5	12,8	280	7,3	10,4	0,4	12,3	1,4
SD3-2,5m	49	1071,8	3,4	-1,5	92,8	60,8	122,6	4,3	144,0	81,8	0,4	550,0	12,3	289	8,7	10,3	0,4	15,0	3,7
SD5-1m		1205,6	4,7	-2,0	102,8	68,8	137,6	4,7	153,0	91,8	1,4	630,0	12,5	304	15,1	13,3	0,5	20,2	2,4
SD5-2.5m	48	1188,2	4,7	-1,0	103,3	68,5	137,1	4,7	153,0	91,3	1,6	613,5	12,1	310	8,9	13,0	0,4	15,6	3,8
SD6-1.3m	37	1267,6	2,3	2,3	119,3	76,2	151,6	4,9	158,5	99,0	1,8	641,0	12,1	326	6,4	12,5	0,6	12,2	1,0
SD8-1.5m	119	1145,0	7,1	-1,6	98,8	65,3	132,6	5,5	142,0	91,8	1,3	593,0	12,2	258	9,0	11,0	0,3	13,2	1,0
SD9-1m	171	1182,0	8,2	0,8	106,5	70,5	142,0	4,7	152,5	95,1	0,1	601,5	12,6	279	15,2	13,7	0,5	20,3	16,8
SD9-5m		1239,2	8,2	-3,6	103,3	67,5	142,1	4,7	155,5	99,4	0,4	652,0	11,6						
SD10-1m	179	1241,4	2,2	0,4	107,8	73,2	153,1	5,0	148,0	105,0	0,9	634,0	11,5	294	8,3	13,8	0,3	8,2	0,6
SD10-4.5m		1309,6	2,0	-2,9	108,8	73,0	154,1	5,0	149,0	104,0	0,4	701,0	11,6	279	8,6	13,4	0,3	8,4	0,8
SD13-4m	260	1294,5	2,1	-2,2	110,8	74,7	150,6	5,0	147,5	105,5	0,3	685,5	11,9	294	17,9	14,9	0,9	21,7	1,4
SD14-5.5m	218	1089,0	2,2	-0,6	100,3	64,4	128,1	4,7	152,5	92,2	0,1	533,0	11,4	230	11,7	11,2	0,5	14,6	16,3
n° sample	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Rb**	**Sr**	**Mo**	**Cd**	**Sn**	**Sb**	**Te**	**Cs**	**Hg**	**Tl**	**Pb**	**Bi**	**Th**	**U**
	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
SD1 1m	0,3	3,6	2,0	1,4	1,8	*1,8*	3141	6,25	0,03	0,09	0,27	0,12	<0,01	0,03	0,07	0,73	0,16	0,05	18,89
SD1 4m	0,4	5,3	2,8	4,3	2,2	2,0	3218	6,81	0,08	0,06	0,27	0,09	<0,01	0,03	0,03	0,68	0,07	0,02	17,71
SD2	0,5	5,1	1,6	2,3	5,1	2,1	3712	11,94	0,04	0,03	0,64	0,11	<0,01	0,04	0,02	0,44	0,04	0,01	11,21
SD3 1m	0,3	4,0	1,3	1,4	3,2	1,8	2550	7,16	0,02	<0,02	0,49	<0,08	<0,01	<0,03	<0,01	0,12	0,01	<0,01	12,44
SD3 2.5	0,3	4,0	1,3	1,7	3,1	1,8	2555	7,15	0,02	<0,02	0,50	<0,08	<0,01	0,03	<0,01	0,08	0,01	<0,01	12,79
SD5 1m	0,4	5,1	2,4	3,1	*3,3*	2,1	2761	7,91	0,05	<0,02	0,52	<0,08	<0,01	<0,03	<0,01	0,16	<0,01	<0,01	13,73
SD5 3m	0,4	5,4	1,5	2,3	3,3	*2,1*	2820	8,25	0,02	<0,02	0,53	<0,08	<0,01	<0,03	<0,01	0,08	0,01	<0,01	14,08
SD6	0,3	4,7	2,4	2,7	2,4	1,9	3055	7,62	0,04	0,02	0,49	<0,08	<0,01	<0,03	<0,01	0,46	<0,01	<0,01	13,36
SD8	0,3	4,2	1,9	1,7	2,0	1,7	2397	7,41	0,04	0,07	0,52	0,11	<0,01	0,03	0,03	0,18	0,15	0,04	13,03
SD9 1m	0,4	5,5	2,4	2,4	2,0	1,9	2553	7,94	0,04	0,02	0,51	<0,08	<0,01	0,03	<0,01	0,11	0,05	0,02	12,92
SD10-1m	0,3	4,8	2,3	1,8	1,8	1,8	2666	7,70	0,03	<0,02	0,51	<0,08	<0,01	0,03	<0,01	0,08	<0,01	<0,01	12,53
SD10-4.5m	0,3	4,7	2,2	1,2	1,8	1,7	2491	7,66	0,02	<0,02	0,52	<0,08	<0,01	<0,03	<0,01	<0,05	<0,01	<0,01	12,23
SD13	0,4	5,5	2,7	1,8	1,9	1,8	2540	8,58	0,03	<0,02	0,54	<0,08	<0,01	<0,03	<0,01	<0,05	<0,01	<0,01	13,27
SD14	0,3	4,6	2,6	2,8	1,6	1,6	2130	7,68	0,03	<0,02	0,54	<0,08	<0,01	<0,03	<0,01	0,18	<0,01	<0,01	11,75

Table 2a. Results of the chemical analyses on water samples from the Syrdarya River - April 2004.

N°sample	Depth	Sampling time	Sampling place	GPS Coordinates			Water Temp.	Elec.Con d. (25°C)	Diss. Oxygen	Redox Pot.	PH	Alkalinity	Equivalent TIC
				Longitude	Latitude	Altit.(m a.s.l.)	(°C)	uS/cm	mg/l	(mV)		meq/l	mg/l
SD1-HE	2m	24/04; 13.45	Bridge upstream Chard-ara reservoir	68° 31'08 E	41°01'78 N		21.2	1319.26	8.22	387.459	8.17	3.23	38.76
SD2-HE	1m	24/04 ; 11.30	Karasakal village, upstr. and south, bank of Chardara reservoir	68° 08'15 E	41° 02'53 N	246	19.7	1295.3	9.02	376.531	8.47	2.80	33.60
SD3-HE	5m	24/04 ; 8.45	Zolotye Pesky, 7 km be-fore Chardara dam	67° 55'48 E	41° 12' 19 N		16	1223.17	9.56	378.173	8.35	3.04	36.48
SD5-HE	1m	23/04; 19.45	Chardara city down-stream from the dam	67° 57'39 E	41° 15'05 N		17.6	1267.61	8.99	403.03	8.22	3.00	36.00
SD8-HE	1 m	22/04 ; 19.40	NearAqkol hamlet, right bank	67° 51* 04 E	43° 09'37 N	168	15.9	1308.07	9.25	390.245	8.25	3.09	37.08
SD9-HE	1m	22/04 ; 14.00	Downstream from Chi-lli, right bank	66° 22' 13 E	44° 16' 31 N	138	13.2	1335.08	9.32	437.173	8.2	3.00	36.00
SD10-HE	1m	21/04; 19.30	Downstream from Kyzyi-Orda, right bank	65° 17' 47 E	44° 59' 26 N	146	13.8	1300.26	9.22	370.744	8.22	3.11	37.32
SD13-HE	2m	21/04; 17.45	Jalagash bridge	64° 33' 05" E	45° 02' 49" N	105	13.4	1291.67	9.94	382.03	8.2	3.08	36.96
SD14-HE	1 m	16/04; 19.00	Karateren bridge	61° 02' 33" E	46° 02' 12"N	40	11.6	1500	10.17	401.316	7.14	3.02	36.24

Table 2b. Results of the chemical analyses on water samples from the Syrdarya River– April 2004.
Legend: TDS: Total Dissolved Salts, SPM: Suspended Particulate Materials, IB: Ionic Balance, LLD: Lower Level of Determination, LLQ: Lower Level of Quantification.

N° Sample	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3	DOC	TDS	IB
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
SD1-HE	112.00	51.60	89.60	4.30	63.50	411.20	185.00	10.20	1.40	930.10	2.50
SD2-HE	104.00	51.70	95.30	4.30	64.80	400.30	160.00	6.60	2.50	889.70	6.44
SD3-HE	104.00	47.00	86.00	4.00	61.10	378.10	175.00	8.40	1.70	866.20	2.72
SD5-HE	108.00	49.40	90.10	4.40	62.60	388.40	176.00	8.60	1.70	890.10	4.98
SD8-HE	101.00	49.60	93.70	4.20	67.30	403.80	180.00	8.50	1.40	910.70	-0.30
SD9-HE	104.00	52.30	100.00	4.20	69.90	400.30	181.00	8.20	1.60	922.50	4.34
SD10-HE	98.00	49.50	95.70	4.00	68.20	377.80	182.00	8.20		885.90	2.84
SD13-HE	101.00	51.20	98.90	4.30	68.30	378.50	184.00	7.90	1.90	896.70	5.74
SD14-HE	105.00	59.30	118.00	5.00	94.00	442.30	183.00	6.00	2.50	1015.50	3.14
LLD	0,1	0,1	0,1	0,3	0,1	0,1	5,0	0,1	0,5		

N° Sample	B	Al	Ti	Cr	Fe	Mn	Co	Ni	Cu	Zn	As	Rb	Sr
	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
SDHE1	192.60	9	32.58	1.77	13	3.63	0.95	19.9	3.39	3.39	2.93	1.70	2493
SDHE2	201.08	17	32.09	1.39	20	3.16	0.92	18.4	3.49	3.96	2.59	1.65	2447
SDHE3	195.30	8	30.49	1.66	13	0.84	0.81	17.9	3.01	3.69	2.48	1.52	2359
SDHE5	189.78	9	31.55	1.61	15	1.49	0.88	18.9	3.12	3.74	2.60	1.57	2371
SDHE8	185.64	29	32.62	1.40	23	1.58	0.82	18.0	3.12	4.14	2.03	1.44	2383
SDHE9	181.12	9	31.87	1.27	14	0.81	0.80	18.4	3.04	3.06	1.98	1.35	2447
SDHE10	152.06	10	26.83	1.00	13	1.34	0.69	15.5	2.52	2.37	1.72	1.14	2325
SDHE13	159.76	7	28.72	0.96	12	1.25	0.75	16.2	2.79	2.44	1.87	1.18	2447
SDHE14	176.36	17	30.75	0.81	17	2.22	0.77	16.5	3.01	2.85	2.09	1.47	2703
LLD	0,02	0,36	0,02	0,03	0,39	0,00	0,00	0,13	0,01	0,02	0,01	0,00	0,02
LLQ	0,07	1,08	0,05	0,08	1,18	0,01	0,00	0,38	0,02	0,06	0,04	0,01	0,05

N° Sample	Mo	Cd	Sn	Sb	Te	Cs	La	Ce	Tl	Pb	Bi	Th	U
	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
SDHE1	10.21	0.08	0.2	0.44	0.2	0.01	0.02	0.04	0.01	0.09	0.02	0.02	18.97
SDHE2	10.32	0.07	0.3	0.44	0.2	0.01	0.02	0.04	0.02	0.15	0.03	0.02	18.43
SDHE3	8.58	0.07	0.2	0.38	0.1	<0,01	0.01	0.02	0.01	0.08	0.02	0.01	15.95
SDHE5	9.21	0.08	0.2	0.39	0.2	0.01	0.02	0.02	0.02	0.09	0.02	0.01	16.96
SDHE8	8.56	0.10	0.2	0.39	0.2	0.01	0.05	0.09	0.02	0.14	0.03	0.02	15.51
SDHE9	8.71	0.09	0.2	0.45	0.1	<0,01	0.01	0.02	0.01	0.06	0.03	0.02	15.66
SDHE10	7.65	0.06	0.1	0.44	0.1	<0,01	0.01	0.03	0.01	0.07	0.01	0.01	13.29
SDHE13	8.16	0.07	0.1	0.49	0.1	<0,01	0.01	0.02	0.01	0.08	0.01	0.02	14.67
SDHE14	8.76	0.06	0.1	0.56	0.1	0.01	0.03	0.06	0.01	0.16	0.02	0.01	15.51
LLD	0,01	0,02	0,04	0,01	0,05	0,00	0,00	0,00	0,00	0,01	0,01	0,01	0,01
LLQ	0,02	0,05	0,11	0,03	0,14	0,00	0,01	0,01	0,01	0,03	0,02	0,02	0,02

Results and discussion

Contribution of the “historic” data

Information concerning Syrdarya River water quality mainly comes from the Hydrometeorological Monitoring Survey of SSR and then Republics of Uzbekistan and Kazakhstan (Hydromet). At least from 1960 to 2002 (and beyond), Hydromet services gathered (even not systematically) water samples from around 24 posts distributed along 2000 km of the Syrdarya River (taking into account only the Uzbek, Tajik and Kazakh parts of the river).

Salinity variation

The SO_4 content can be considered as a reliable index of the water salinity as it tightly correlates with the TDS (Total Dissolved Solids). Three Hydromet posts distributed from the upper reaches of the river (near the Kyrgyz- Uzbek border) till the Uzbek - Kazakh border downstream, were selected. Data were collected there during a relatively long time, with shortest and scarcest interruptions. The latter were nevertheless significant: complete stops from 01/1985 to 12/1993, during 1995 and furthermore there was a systematic gap of November - December data during the first decade (1961-73).

It can be observed (Fig.1a and b) that the SO_4 concentrations roughly grow up

- from up (Kal) to downstream (Chinaz)
- from the High to the Low water period, the SO_4 content being controlled by dilution
- during the first decades (1960 to 1990)

This last trend is consistent with the increase of TDS content in the precipitations: from 24 mg/l in 1968-69 to 157.7 mg/l in 1979-80 (Letolle and Mainguet, 1993).

During the 90's the SO_4 content keeps on growing during the low water periods but starts to decrease during the high water periods. The last data (2000-2002) show a general decrease.

Long period data are lacking on the Kazakh course of the Syrdarya River. Thus the comparison of our data to the previous ones must be cautiously done:

- our data are time limited but not averaged
- the nearest sampling place (Chardara on the Fig.1a and b) from the post of Chinaz.(at about 60 km downstream) may be marked by a higher TDS content as it is located downstream from the confluence with the Chirchik River coming from the Tashkent valley.

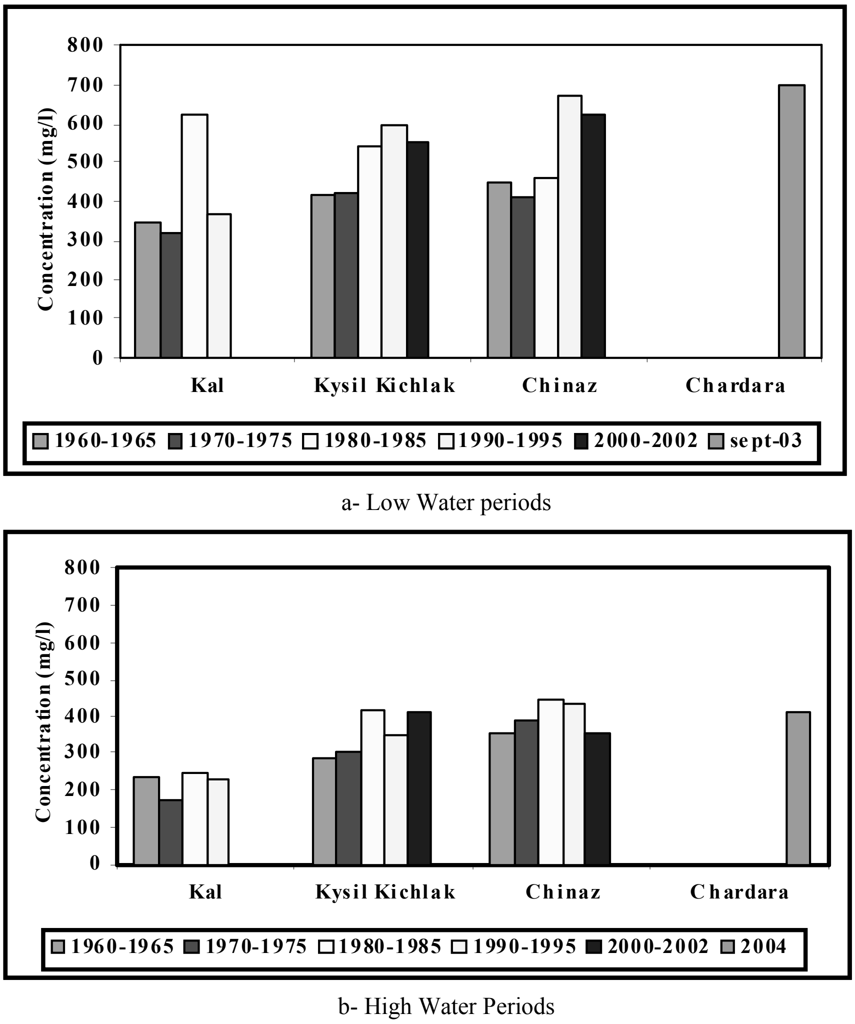

Figure 1. Evolution of the SO_4 concentrations during the 45 last years in the Syrdarya River .

Thus the SO_4 contents of the analysed sample - upstream the Chardara reservoir - are consistent with the spatial increase (from up to downstream) but it cannot be concluded whether there is a new increase with respect to the previous data in the post of Chinaz or if it is merely due to the sample location.

Heavy metals

Annual reports of the Uzbek "Glavhydromet" mentioned average analyses of some monitored heavy metals (Cr, Cu and Zn). The number of samples is not known nor, mostly, the sampling places.

Those monitoring values (Table. 3) cannot be considered as representative of the whole period 1960 – 2001 (and especially of the 30 first years). The most ancient data (1983) are probably influenced by the accident that occurred at the Almalyk copper enrichment centre. The comparison with our data seems consistent with a constant decrease of zinc, a similar range of variation for chromium and a new copper increase. This last trend is nevertheless contradicted by the detailed analyses of Bragin *et al* (2000) (Fig. 2). Conversely, our data rather fit well with their conclusion of a general decrease of the heavy metals in the Syrdarya delta region.

Kochenov and Baturin (1967) analysed uranium from water samples collected in 1965. They found that the uranium content in Syrdarya River (in the delta zone) was 10 µg/l. It largely coincides with our recent results: 11 - 19 µg/l.

Table 3 Evolution of the Syrdarya River water Cr, Cu and Zn contents (µg/l) in the last years

	Uzbek Hydromet data					Our range of data
	1983	1990	1994	1996	2001	Sept.2003 – Apr.2004
Cr	12	1.6	1.7	0.3	1.4	0.3 – 1.8
Cu	79	3.9	1.9	0.8	0.8	1.3 – 3.5
Zn		13.6	14.1	7.2	5.6	2.4 – 4.1

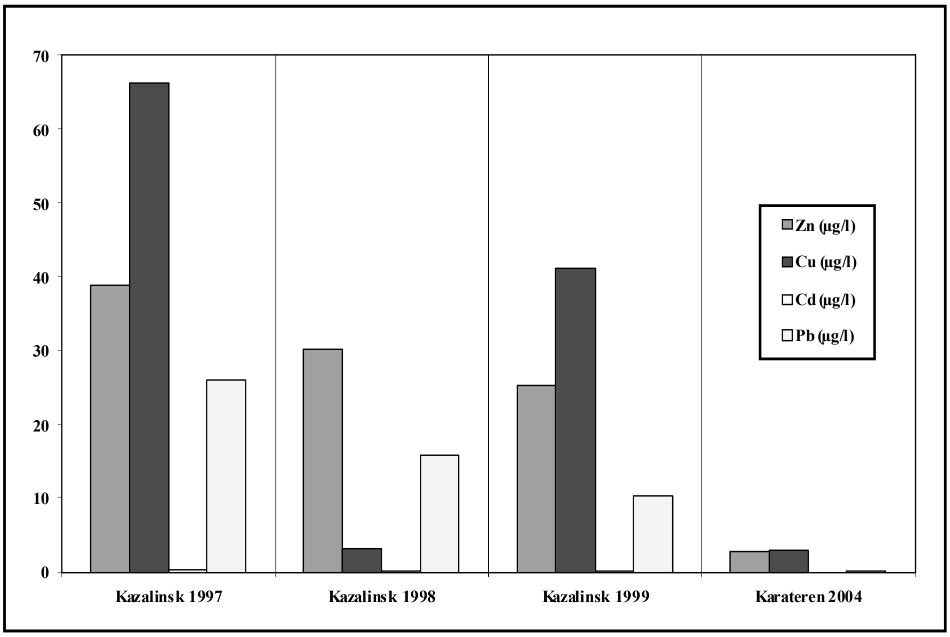

Figure 2. Heavy metals concentration/time in Syrdarya River delta zone (our data and Bragin et al., 2000).

River chemical trends

Seasonal variations

The seasonal variations of the Syrdarya River are mitigated by a series of facilities. The river is regulated by three dams and reservoirs: Toktogul in Kyrgyzstan, Kayrakum (15 km^3) and Farkhad (2 km^3) in Tajikistan and Uzbekistan, and Chardara in Kazakhstan (0.8 km^3). The overflow reservoir system of the Arnasay lakes (joining three previous lakes: Arnasay, Aydarkul and Tuzkan) has a volume varying between 7.4 and 25 km^3 according to the season.

Furthermore several systems of irrigation and drainage canals, reservoirs and discharge lakes along the Syrdarya River and in its delta impact the river regime.

The river flow rates measured by the hydrological posts of Kazhydromet (S. Kotleupov, pers. com.) in three points of the Syrdarya reaches coincide with three of our sampling times and places during both campaigns: Chardara city, Kyzyl-Orda and Karateren (Fig. 3a and b).

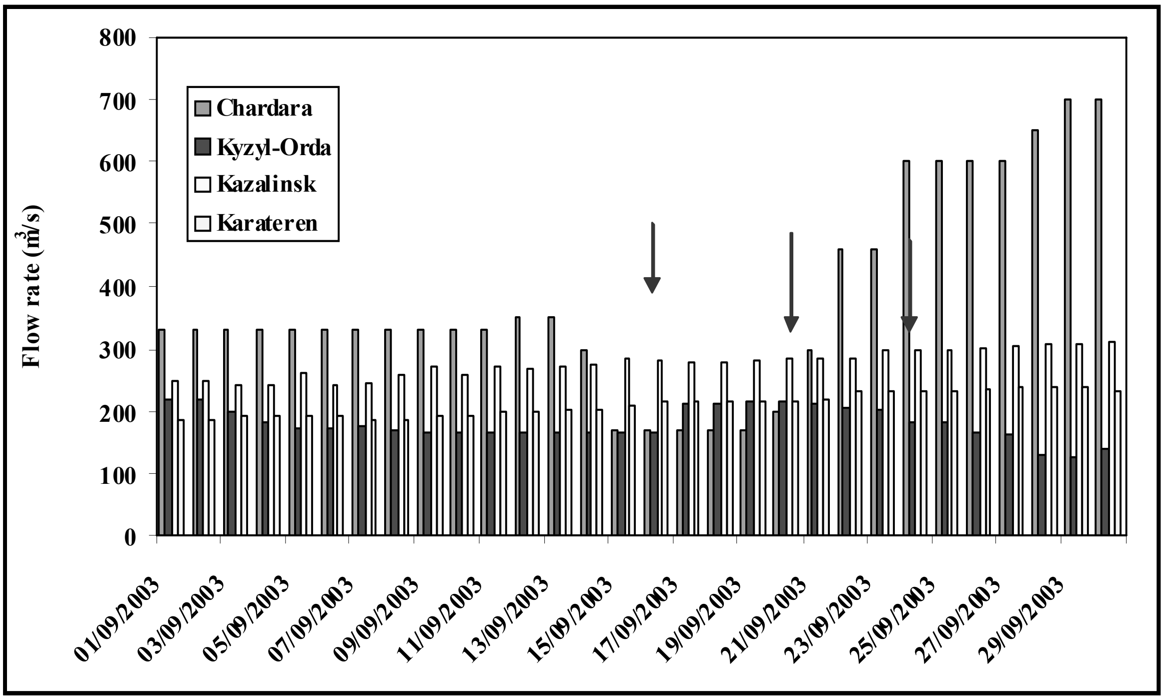

Figure 3a. Flow rates of the Syrdarya river (Sept. 2003).

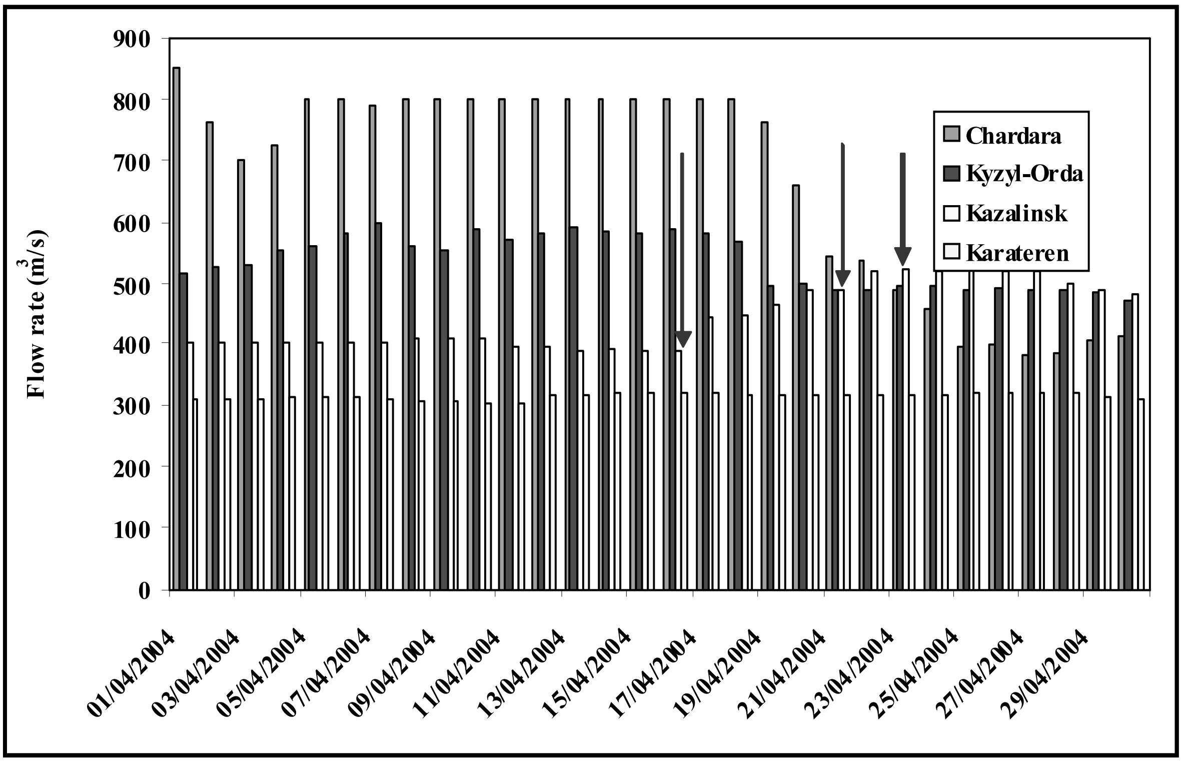

Figure 3b. Flow rates of the Syrdarya river (Apr. 2004).

Dilution trend

Dilution was already mentioned when considering the historic data (Fig 1a and b) and is clearly responsible of the TDS variations (Fig.4).

Environmental variations

Besides dilution, environmental variations influence the chemistry of the river water.

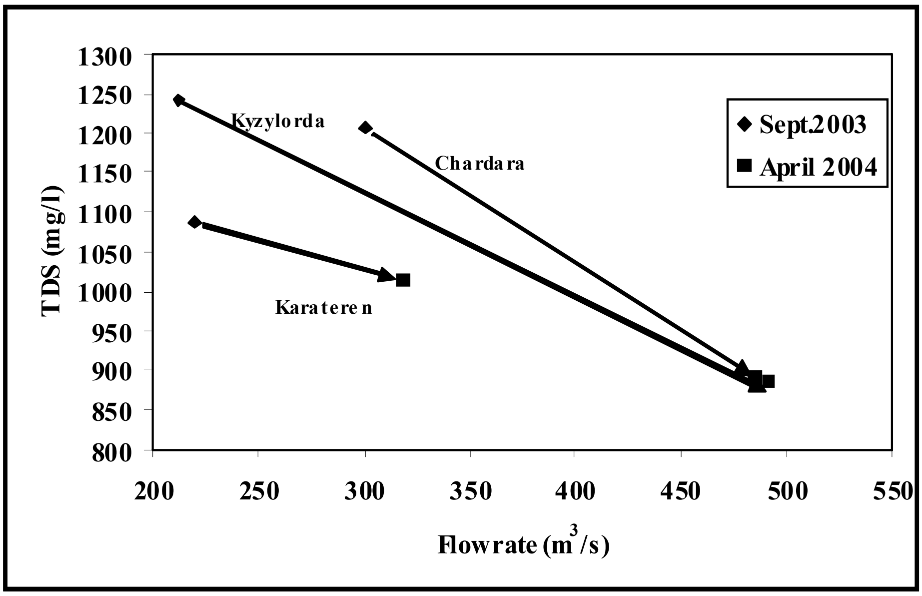

Figure 4. Syrdarya River TDS content / Flowrate.

Temperature

The water temperature varies with depth and day time but generally speaking the seasonal variations of the water temperature are stronger downstream the Chardara dam (the double in average). The temperature variation contributes to several other consequences.

Biomass

Chardara dam marks also a difference in the SPM composition. As most of the solid mineral phases settle down, an increase of phytoplankton can be inferred there from several parameters.

The diurnal variations of the dissolved oxygen and of the river water pH, near the Chardara reservoir and downstream from it are consistent with phytoplankton photosynthesis / respiration rhythms: oversaturation in dissolved oxygen and higher pH (in spite of higher temperature) at the end of the day and conversely low oxygen concentration and relatively low pH values early in the morning. The role of the phytoplankton was studied by Mamatov and Shirikova (2001) in the neighbouring Lake Arnasay (overflow of the Chardara reservoir): they observed diurnal oversaturations of dissolved oxygen (till 150%) and a nocturnal drop by a factor 2 or 3. A similar trend toward eutrophication was found here.

Carbonate system

Another consequence of average temperature variation is the correlated variation in HCO_3 content. According to our data, the Syrdarya River water is controlled by the bicarbonate equilibrium; so when temperature decreases (from September 2003 to April 2004) the equilibrium moves and more bicarbonate is dissolved.

This trend concerns Ca, Mg and Sr as well. A similar trend has been observed in the Loire River (Grosbois, 1998).

Metals

A striking aspect of the seasonal variations of the Syrdarya River composition is the increase in different dissolved metals from September to April in spite of a general decrease of the TDS (by around a factor of 1.5), confirming that those species are not merely controlled by a dilution phenomenon. Some trace elements increased by factors from 2 to 4 (Ni, Ti, Sn, Cu and Co) some other less (Cr, Zn, Mo, Cd, Te and U). Conversely others (Fe, Mn, Sb, Pb, As, Rb, Cs,…) decreased from September to April (Tab.1b and 2b). It is thus supposed that phytoplankton in September plays a better role as a filter than in April. Bragin and Matmuratov (1994) already stressed the role of phytoplankton in the Chardara reservoir as a bioaccumulator of heavy metals.

It may be assumed that those variations result from the leaching of either the upstream mining areas (in Uzbekistan and Kyrgyzstan) or the agricultural wastes (Bragin and Matmuratov, 1994) when snow melts.

Nitrate

The nitrate concentration grows up from September to April by a factor of around 5 for most of the samples (except SD1 that remains at 10 mg/l). Those analytical results show that nitrates fertilizers, at least, are used at the end of wintertime. Mamatov and Shirikova (2001) observed in the Lake Arnasay that the concentration in nitrogen compounds is higher at spring than in autumn.

Spatial variations

Variation with depth

The depth of Syrdarya River bed in Kazakh Priaralie varies between 5 to 10 m. Differences are significant (in September) only in the Chardara reservoir or just up and downstream from it: Mn and Fe contents, at least, grow up as the redox potential decreases from the superficial to the deeper sample.

Variation from up to downstream

The main source of spatial as well as seasonal variations is the Chardara reservoir.

TDS drop

The TDS of the river water dropped down by 18% in September and 4% in April when it passed the Chardara reservoir (Fig. 5). Two causes could explain this decrease. In September 2003 the pH variations due to Phytoplankton photosynthesis, the higher temperature and the lower flow rate of the waters favours the (1) carbonate precipitation or (2) consumption by the biomass. HCO_3 content decreased then in 37%, Ca in 45%, Sr in 27% and Mg in 14%. The other decreases of major elements (like some SiO_2 scavenged to build the diatomea shells) may also be due to consumption by the biomass.

Chardara denitrifying action

The decrease of NO_3 content especially in September 2003 (by a factor of 10) in the Chardara reservoir confirms the role of phytoplankton as a denitrifying agent. It can be noted that in April 2004 the NO_3 content increased again downstream from the reservoir probably as a result of both the agricultural practices of the surroundings and the lesser biomass.

The higher values in nitrate content upstream from Chardara reservoir in September 2003 may result both from a more intensive use of fertilizers in the upper part of the Syrdarya valley (from the Chirchik tributary or from the Fergana valleys) and from the waste waters of the city of Tashkent.

Chardara filtrating action

Most of trace elements do not decrease significantly after crossing the reservoir (a few of them as Ti, Mo and Sb even increased in September 2003). A group of metals (Mn, Cr and U) clearly dropped in both seasons. Then some elements decrease in April 2004 and not in September 2003 (Co, Ni, Cu, As, Rb) and vice versa (Sn, Pb). The reservoir seems to act as a selective, limited and seasonally changing trap for heavy metals.

Bragin and Matmuratov's analyses (1994) show that phytoplankton accumulates first Zn, then Cu, Pb and Cd (they analysed a more limited range of elements).

Delta lakes influence

In the delta zone, in April, when the Syrdarya River floods and connects with lakes, the river may be impacted by them. DOC of the Syrdarya River increases and NO_3 decreases in relation to the growth of phytoplankton. Furthermore TDS reaches its maximum as those lakes are mostly salted ones and / or drainage outlets like Kamyslybas.

Industrial and urban impact

The pollution impacts of the different cities, of the Arys River and of the drainage canals net (including the Arys – Turkestan system) can be detected especially in September by the increasing contents of DOC and SPM, by low oxygen concentrations. The most significant (albeit not strong) other impact of an urban contamination was detected in September downstream from the Chi-Ili city where contents in Dissolved Organic Carbon, Mn, Fe, Al and, at a lesser degree, Ni grew up.

Water quality

The Syrdarya River samples comply with the local and international standards except for TDS and Mn and mainly in September 2003. None was concerned by excess with neither NO_3 nor heavy metals versus local and/or European standards (European Commission Directive 98/83/CE of 03/11/1998).

Beyond the comparison with the standards, Syrdarya River water composition can be compared with other rivers of the world (Tab. 4). Taking into account that we are comparing average values and intervals (our data), it appears that Syrdarya River chemical composition is similar to the other rivers particularly with the Seine River. It has all the same two peculiarities with respect to other mentioned rivers: lower Fe, higher Sr and, at a lesser extent, Ni contents. The abnormally high Sr content, at least, is very likely due to regional geochemical anomaly as no anthropogenic Sr source is identified.

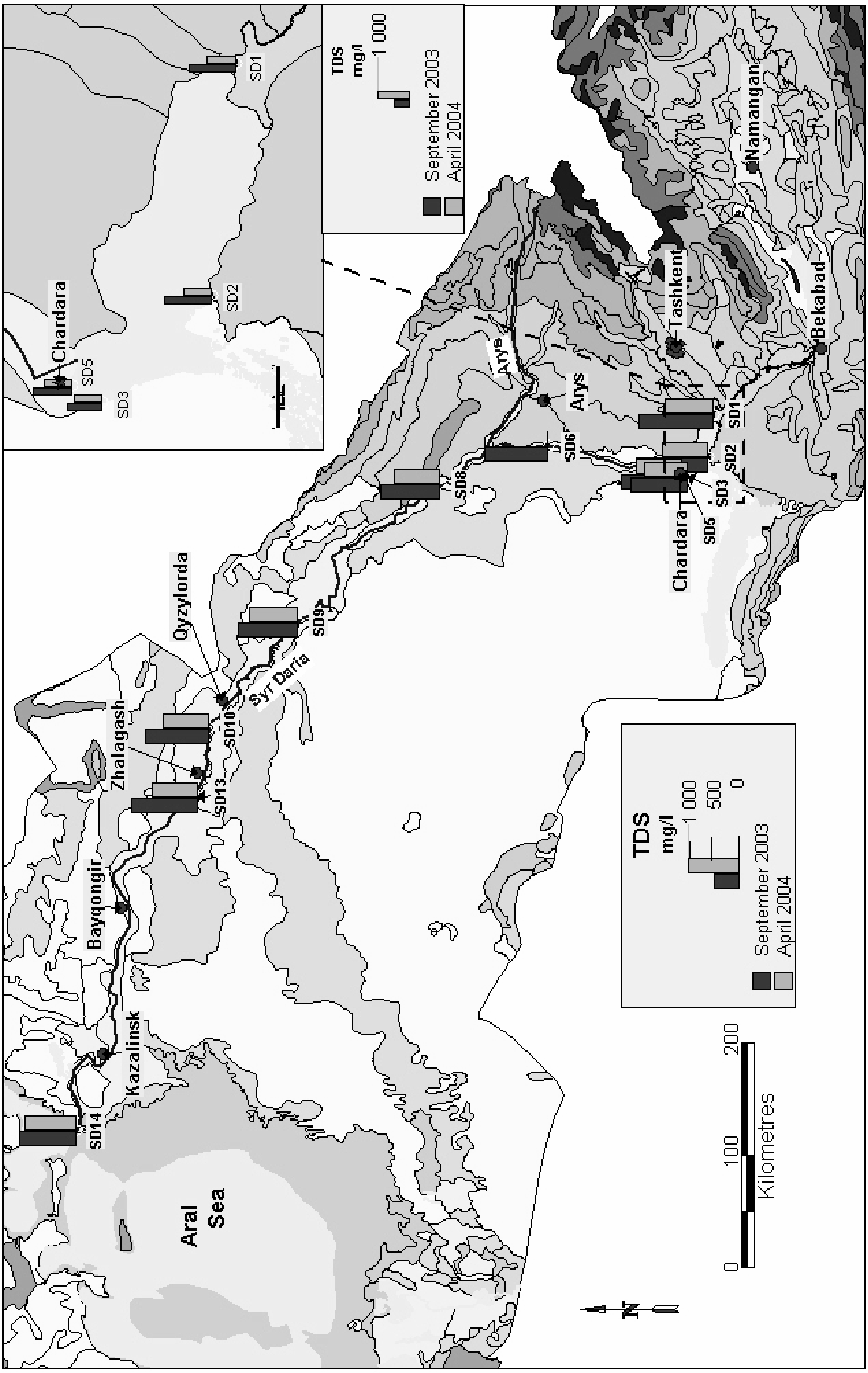

Figure 5. Total dissolved solids (TDS) in water samples of Syrdaria. River.

Table 4. Abundance of trace elements in various rivers of the world in µg/l (from Grosbois, 1998).

Element	Loire	Seine	Amazone	Congo	Mississipi	Yangtze	Syrdarya
Fe	63,78	331,45		179,16			8,20 - 25,20
Rb	3,42	0,95	0,98	2,07	0,78		0,77 -1,37
Sr	98,57	210,38	16,42	8,77			1357,58 - 1947,16
Mn	3,08	2,12	52,38		0,71		0,61 - 16,57
Pb	0,73	0,07 (0,13)	0,02		0,00		0,01 - 0,20
Cu	3,43	1,84 (1,51)	1,28		1,59	1,12	1,14 - 3,07
Cr	3,69	0,89	0,04	0,54	0,08	0,17	0,32 - 1,90
Zn	4,12	3,29 (7,87)	0,95		0,24	0,06	1,20 - 3,67
Ni	3,87	4,24	0,67	0,95	1,68	0,17	3,42 - 18,93

Conclusions

Relatively good agreements were found with the former scientific data concerning the decrease of the Heavy Metals contents of the Syrdarya River. The increase of the salinity linked to the regional aridisation, including a salinisation of the soils and of the precipitations could not clearly be demonstrated for the river during the last decade.

The inorganic pollutants of the current Syrdarya River are influenced by several phenomena:

- a lot of heavy metals (Ni, Ti, Sn, Cu, Co,…) probably coming from the leaching of upstream mining areas or agricultural wastes during the snow melting at spring
- phytoplankton, enhanced by the summer temperatures, the lower flow rates and probably by a new increase of nitrates, grows in the Chardara reservoir and consumes part of the salt content, nitrates, silica and some heavy metals in the low water period
- various discharges contribute to the pollution of the river. Besides agricultural fertilizers (NO_3,…), the urban waste waters (bringing SPM, DOC, lowering the oxidation level of the water,…) and some industrial (present or passed, local or upstream) activities may impact the river water quality.
- the geochemical regional background influences the composition of the river (Sr abnormal concentrations)

The water quality of the Syrdarya River currently complies with local and European Standards except for TDS and locally for Mn mainly in September.

Additional studies including our data concerning river SPM and sediments, other water bodies of the Kazakh Priaralie and geochemical modelling would allow to precise the origins and the fates of the inorganic pollutants by taking into account the hydrobiogeochemical reactions involving them.

Syrdarya River will play an important role in the future quality of the renewed Small Aral Sea as well as of the irrigation and drinking waters. The passed experience showed that it quickly moves and a serious monitoring of the river quality is a basic condition to improve the regional ecologic and economic situation.

Aknowledgements

We are grateful to K. M. Pachikin, R. M. Nasyrov, O. G. Erokhina from the Soils Institute of the Kazakh Academy of Sciences, to M. Iliushchenko and H. Mukhamedzhanov from the Chair of Environmental Chemistry of the AIPET University, to S. Kotleupov from the Institute of Geography in Novokazalinsk and J.P. Roux who efficiently helped in the implementation of the field campaigns in the Kazakh Priaralie.

References

Bragin B., Matmuratov S., 1994. Modern ecological and toxicological situation in the lake system of the Syrdarya delta.

Bragin B.I., Sokolov S.B., Jashenko R.V., 2000. Accumulation of heavy metals and chlorine organic pesticides in components and trophic chains of water areas of the Syr-Darya River delta and human diet. *Ecological Research and monitoring of the Aral Sea deltas, A basis for restoration, book 2, UNESCO Aral Sea project, 1997-2000 final scientific reports: 55-70.*

Grobois C., 1998. Géochimie des eaux de la Loire: contributions naturelles et anthropiques, quantification de l'érosion, *Thuse de doctorat de l'Universitй de Tours: 1-232.*

ISO 5667-1: Guidance on the design of sampling programmes – Technical Corrigendum 1, 1996 – 02 - 01

ISO5667-2: Guidance on sampling techniques – Technical Corrigendum 1.

ISO5667-3: Guidance on the preservation and handling of water samples, june 2004.

ISO5667-4: Guidance on sampling from lakes, natural and man-made, 1987.

ISO5667-6: Guidance on sampling of rivers and streams, 1990-12-15.

Létolle R., Mainguet M., 1993. Aral, *Springer Verlag France.*

Mamatov S.A., Shirikova Yu.I., 2001. Lakes hydro - environmental composition in the Republic of Uzbekistan (on the example of Arnasay lakes system). *SANIIRI report, Tashkent: 1-6.*

Savenko V.S., Kulmatov R.A., 1997. Trace elements in the sedimentary material of the Aral Sea Basin. *Geokhimiya, 11: 1161-1163*.

Received 30 November 2005

Резюме

Гадалиа А., Мотелика-Хейно М., Сера Х., Абу Акар Аффр, Джоун Ф., Чарпи Э. **Неорганические загрязнители реки Сырдарья (Казахстанское Приаралье).**

Статья посвящена проблемам Аральского Моря и реки Сырдарья. Проведены две интересные экспедиции и уникальные измерения содержания неорганических загрязнителей по всей казахстанской части течения реки Сырдарьи в рамках проекта INTAS – 1072.