HUMAN PERTURBATIONS OF RIVER INPUTS TO OCEANS?AN EXAMPLE FOR HEAVY METALS

Michel Meybeck

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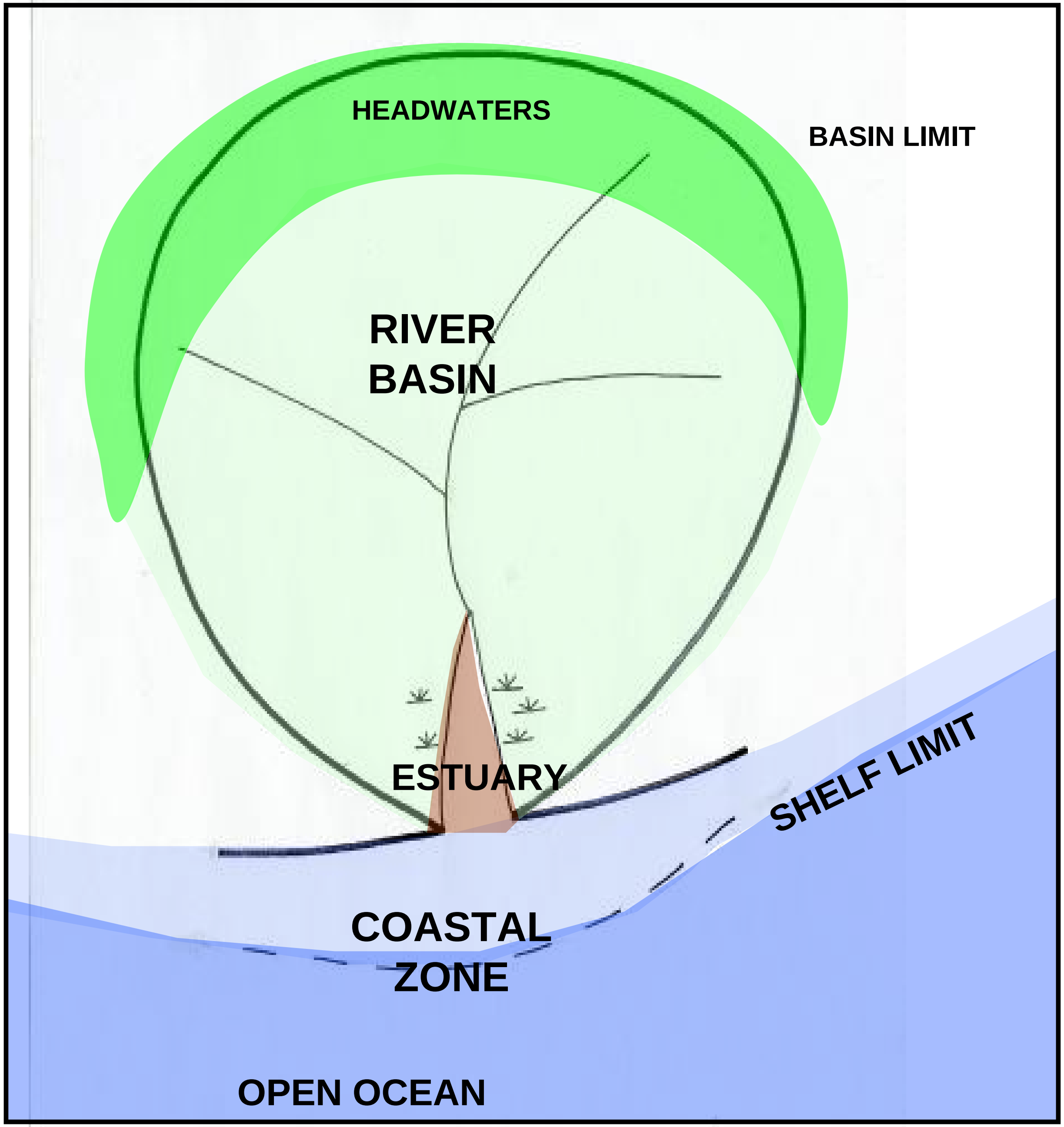
- **PRIVILEGED POSITIONS OF ESTUARIES**
- **HOW TO DEFINE PRISTINE METAL LEVELS**
- **THE PRESENT CIRCULATION OF METALS IN RIVER BASINS :**
- **THE SEINE EXAMPLE(France)**
- **HOW STABLE IS THE METAL CONTAMINATION**
- **HUMAN PRESSURES AND BASINS RESPONSES**
- **GLOBAL BUDGETS:PRISTINE vs CONTEMPORARY**

- **Focus on Cd,Cr,Cu,Hg,Ni,Pb and Zn**

Topology of natural river basin / estuarine system

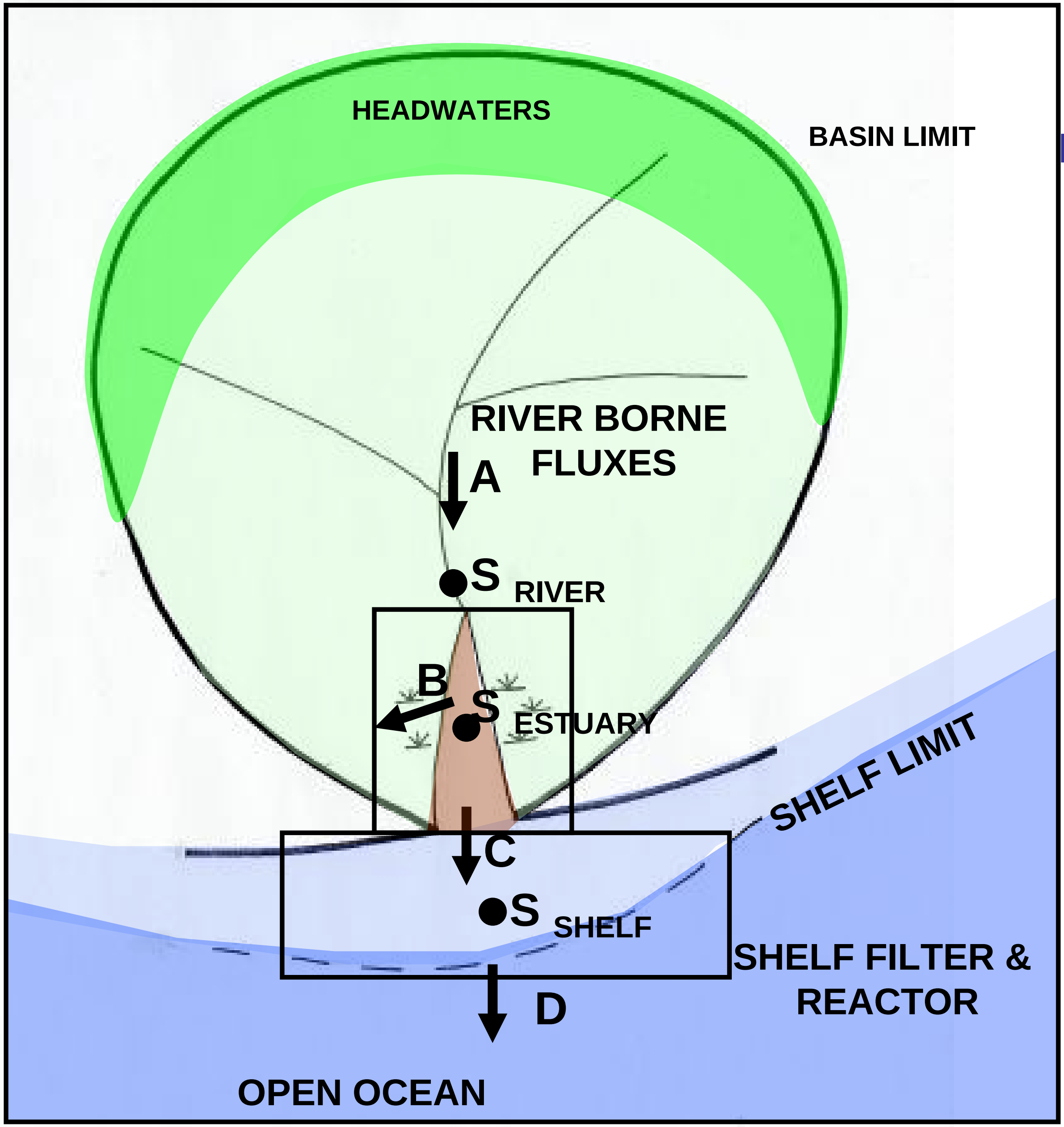


(EARTH SYSTEM SCIENCE)

THE ESTUARY CORRESPONDS TO THE RIVER AND SEA MIXING:WATER AND ENERGY

IT CONNECTS THE RIVER BASIN TO THE COASTAL AREA

Topology of natural river basin / estuarine system

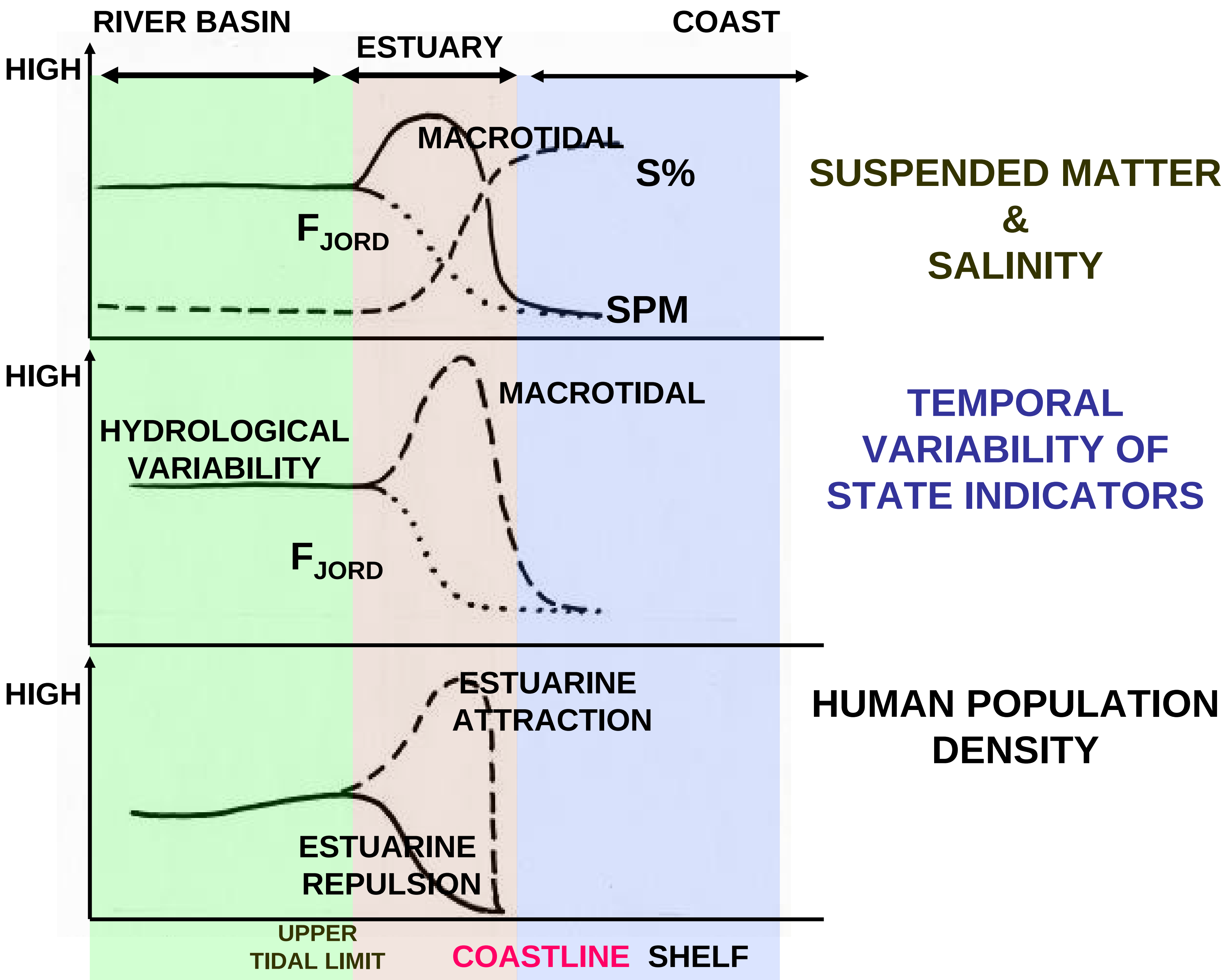


(EARTH SYSTEM SCIENCE)

RIVER BORNE FLUXES(A) ARE PROCESSED AND STORED(B) IN THE ESTUARINE FILTER THEN IN THE SHELF FILTER(C-D)

CONTROL STATIONS CAPTURE THESE CUMULATED INFLUENCES

Longitudinal gradients in estuaries depend on their types



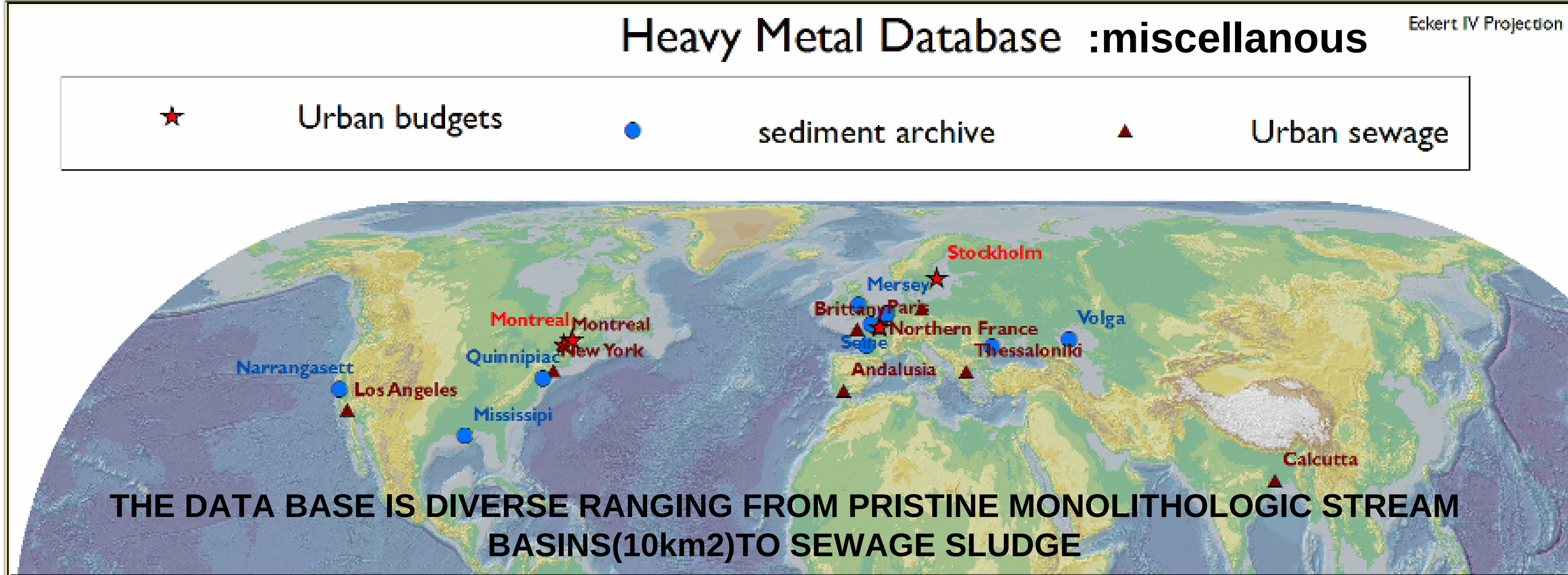
AVERAGE RIVER METAL CONTENTS mg/kg or ppm

	Cd	Cr	Cu	Hg	Pb	Zn
GORDEEV LISITZIN 1979	0.7	130	80		147	310
MARTIN MEYBECK 1979		100	100		150	350
FORSTNER SALOMONS 1980S	0.2	60	25		15	105
MARTIN WINDOM 1991	1.2		100		35	250
Cheng and Wang 1995	0.2	76	50		15.9	107.7
MAC LENNAN 1999	1.0		100		150	350
GLOBAL MODEL THIS WORK	0.30	75	25	0.04	25	90

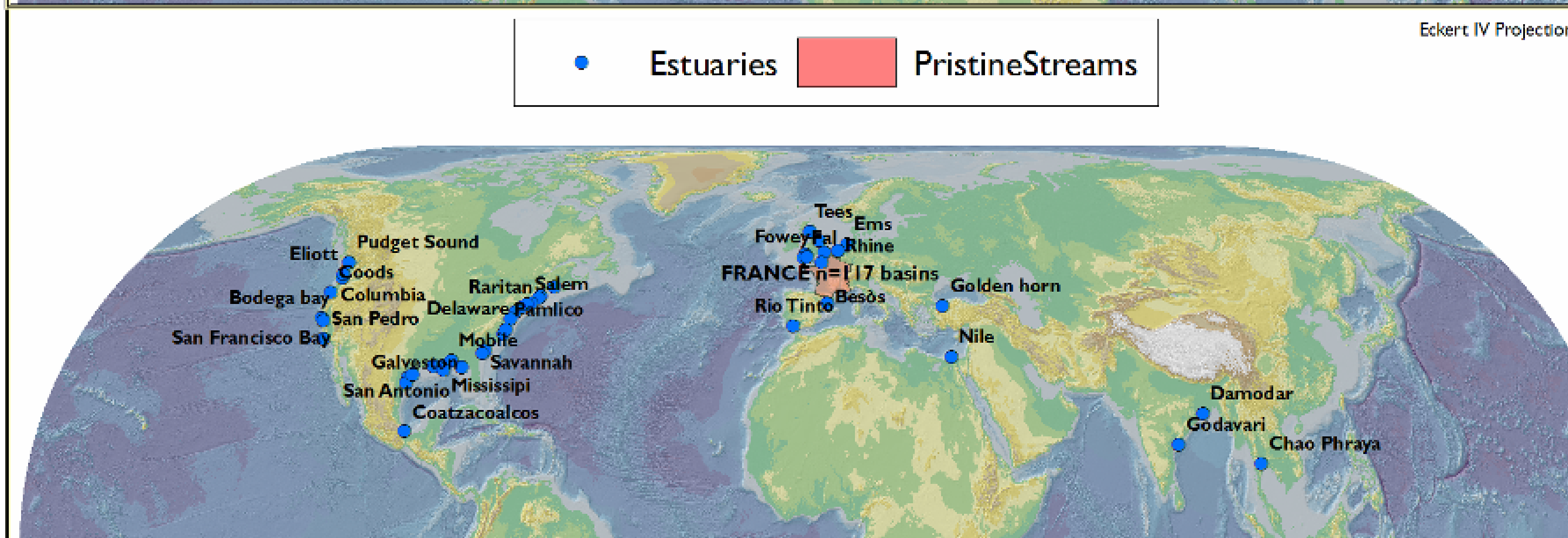
- RIVER CONTAMINATED RIVERS ARE MIXED WITH PRISTINE RIVERS
- RESULTIND IN LARGE VARIATIONS
- FORSTNER LEVELS ARE FROM SEDIMENT ARCHIVES IN W.EUROPE

DATA BASES USED

- Selection of world pristine rivers and tributaries(L=178)from the literature
- Data base on world rivers(L=800)
- Small monolithologic pristine streams in France(N=117)
- Set of estuaries(N= 98)
- Harbours(N=23)
- Sewage treament plants(N=20)



THE DATA BASE IS DIVERSE RANGING FROM PRISTINE MONOLITHOLOGIC STREAM BASINS(10km2)TO SEWAGE SLUDGE



ABOUT 100 ESTUARIES HAVE BEEN CONSIDERED

117 FRENCH PRISTINE STREAMS ARE USED

AFRICA AND SOUTH AMERICA ARE POORLY DOCUMENTED

World river particulates chemistry :data base

LARGE RIVER BASINS ARE NOW BETTER DOCUMENTED THAN IN 1979.

THEY COVER A WIDE RANGE OF CLIMATIC,LITHOLOGIC,AND RELIEF CONDITIONS.

Eckert IV Projection

IN MANY BASINS BACKGROUND CHEMISTRY IS NOW DIFFERENT FROM PRESENT DAY CHEMISTRY

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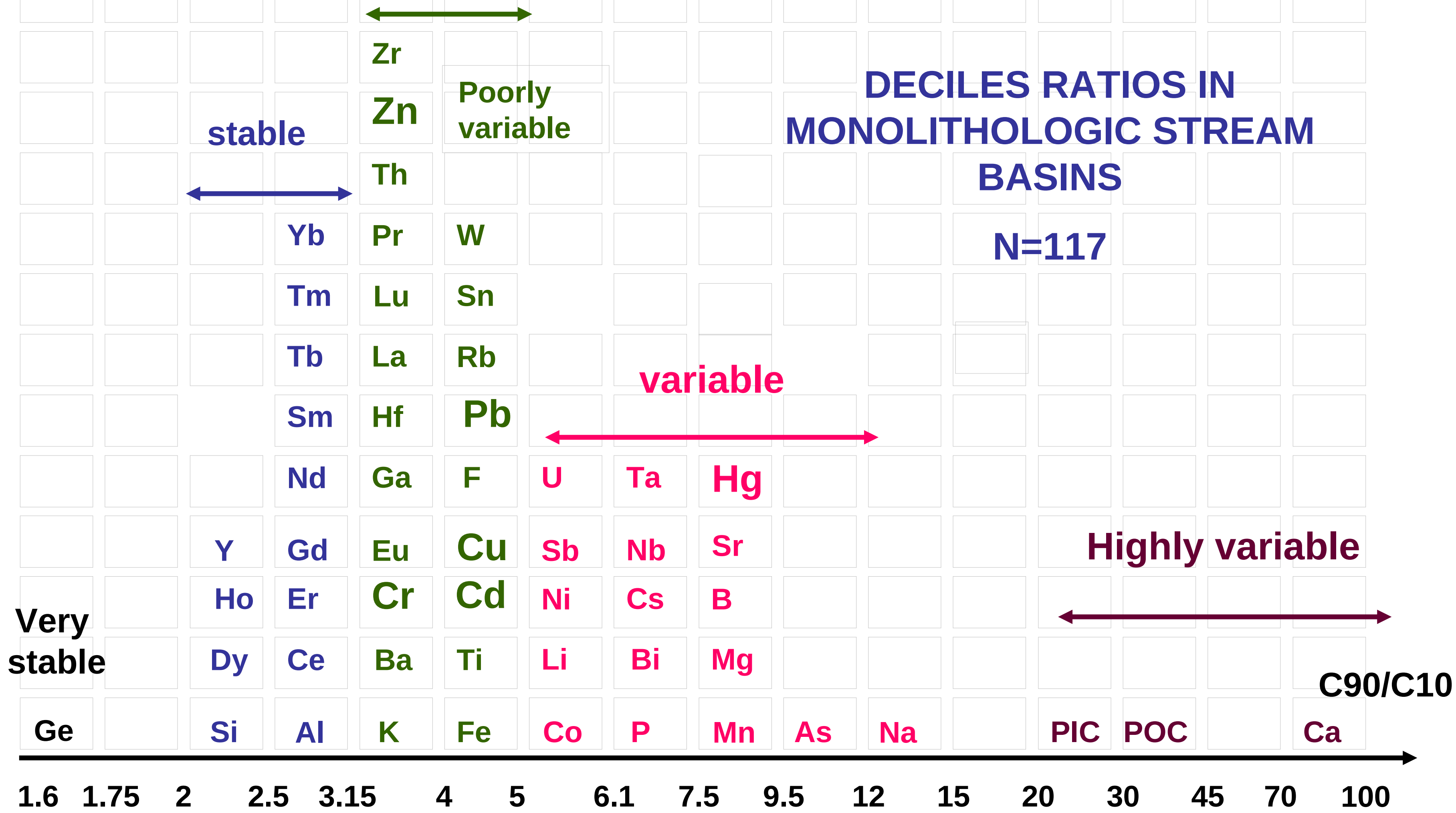
GUILIN KARST LANDSCAPE (SOUTH CHINA)

EACH TYPE OF LITHOLOGY CAN BE CHARACTERIZED BY A SPECIFIC COMPOSITION OF RIVER PARTICULATES.

LIMESTONES HAVE THE LOWEST CONTENTS OF HEAVY METALS TOGETHERWITH SANDSTONES BASINS

NATURAL VARIABILITY OF ELEMENTAL CONTENTS IN RIVER PARTICULATE

(ALL LITHOLOGIES EXCEPT ULTRAMAFIC)



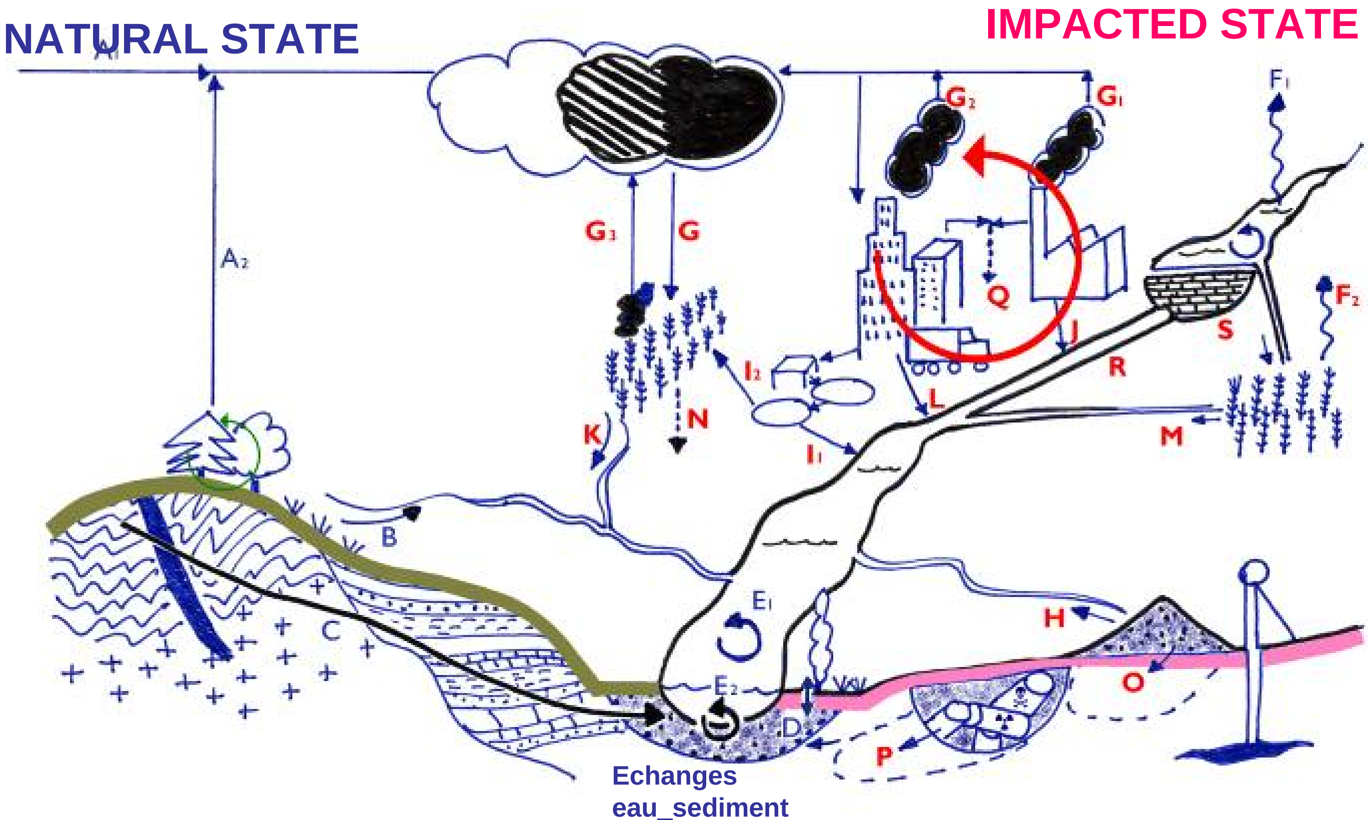
Mercury is naturally more variable than other heavy metals,depending on POC

AVERAGE RIVER METAL CONTENTS (this work)

mg/kg or ppm

	Cd	Cr	Cu	Hg	Pb	Zn
WORLD PRISTINE RIVERS Caverage	0.37	85	31	0.08	25	102
WORLD PRISTINE RIVERS Cmedian	0.27	72	25	0.040	23	90
FRENCH PRISTINE STREAMS Caverage	0.47	94	17	0.045	31	83
FRENCH PRISTINE STREAMSCmedian	0.42	60	15	0.036	23	75
GLOBAL MODEL	0.30	75	25	0.04	25	90
SHALES	0.25	100	45	0.18	22	100

ORIGINS AND PATHWAYS OF METALS IN RIVER BASINS



NATURAL CYCLES

METAL FLOWS IN THE ANTHROPOSYSTEM

IN IMPACTED SYSTEMS BOTH ACCELERATED FLUXES AND MATERIAL RETENTION(reservoir trapping° ARE

THE SEINE RIVER CATCHMENT

- **Area: 65 000 km²**
- **Runoff: 200 mm/y**
- **Population density < 30 p/km² Upper Seine**
  250 p/km² Lower Seine
- **Total Population 17 Mp**
- **Paris Megacity: 10 Mp for 2 500 km²**
- **One giant sewage treatment station for 8 Mp (now 7 Mp)**
- **Multiple industries around Paris and downstream**

LAND USE FOR THE SEINE CATCHMENT
(Corine land cover)

ESTUARY

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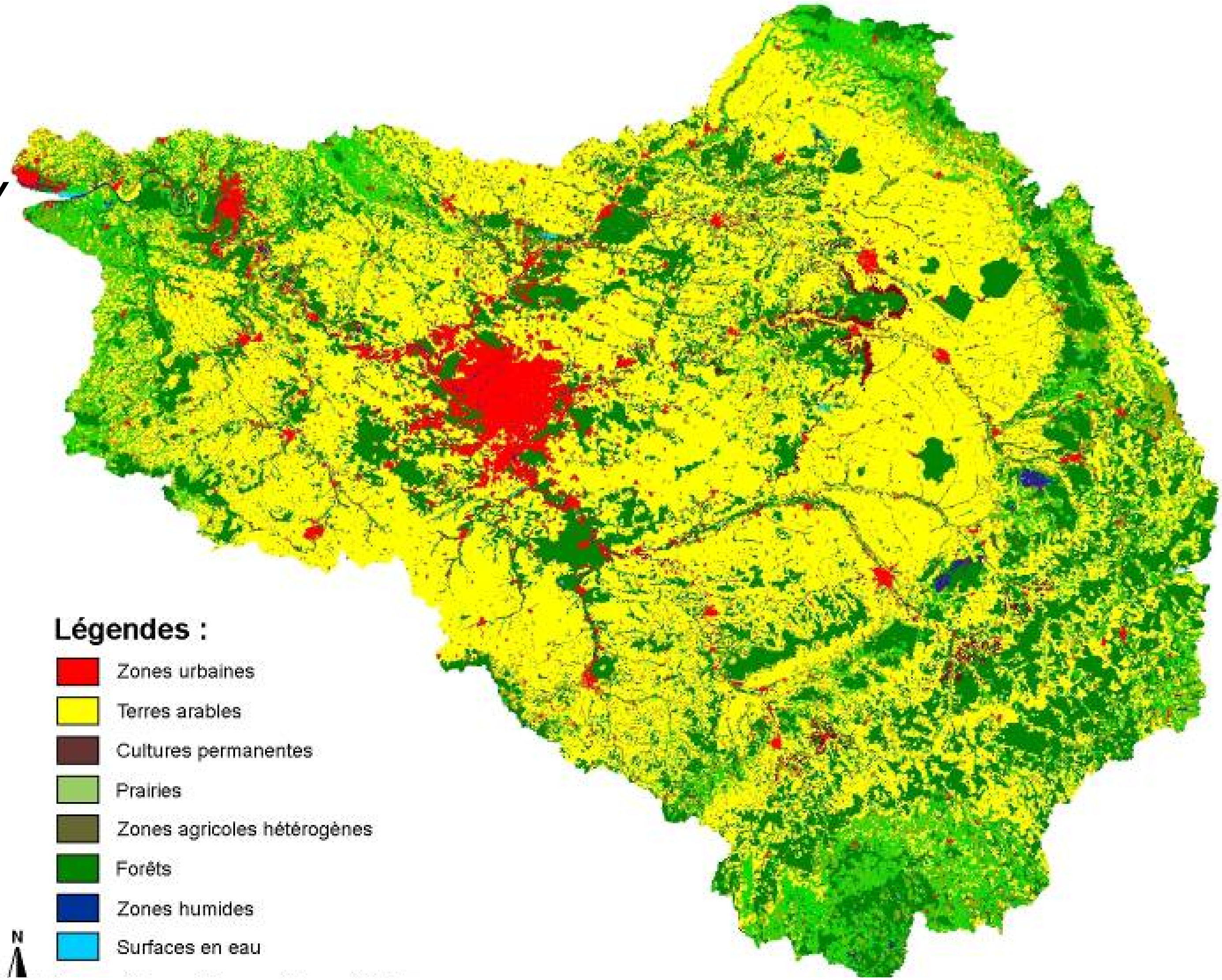
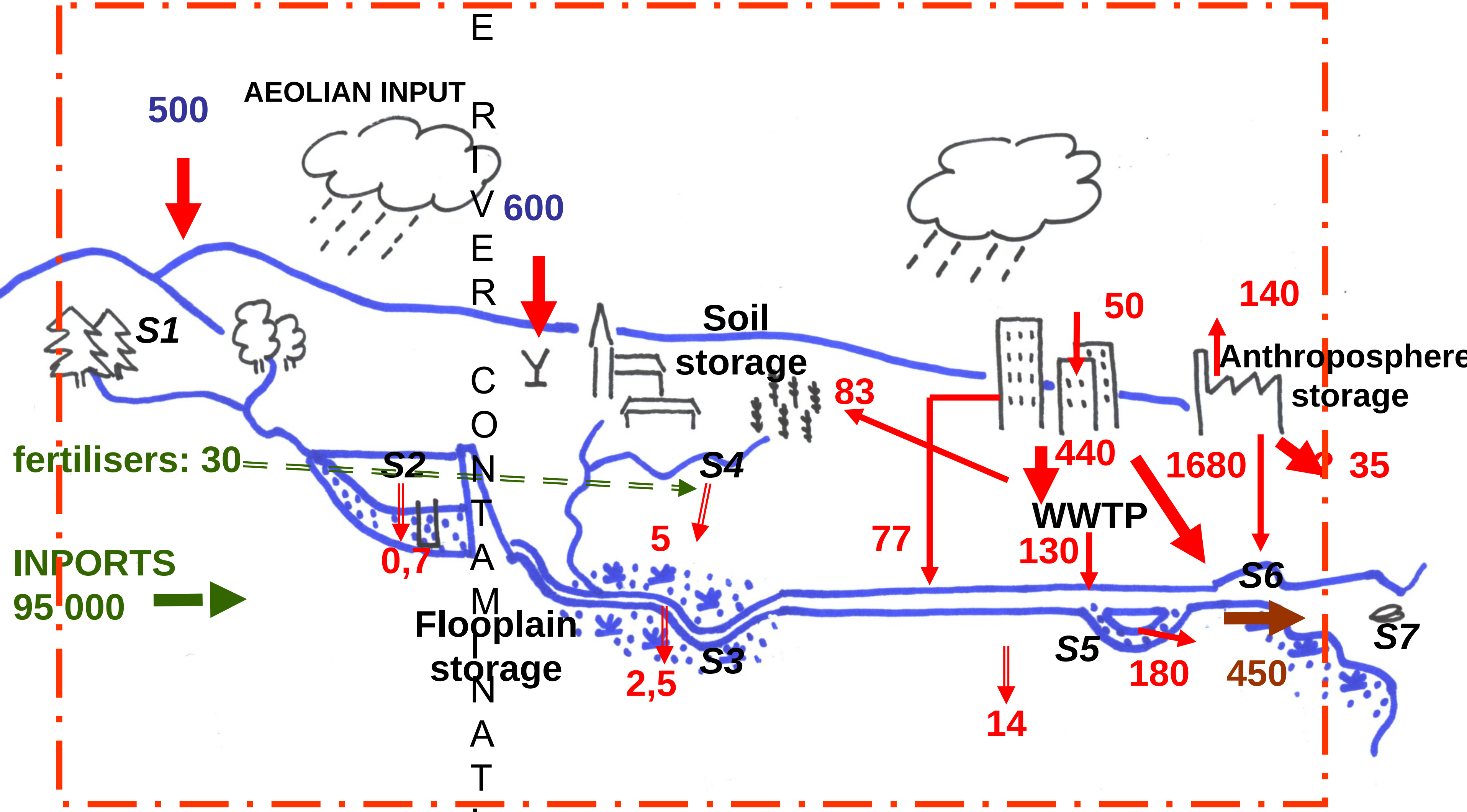


- Urbanized area (red) cropland (yellow) pastures and forest(green)

SEINE RIVER CONTAMINATION

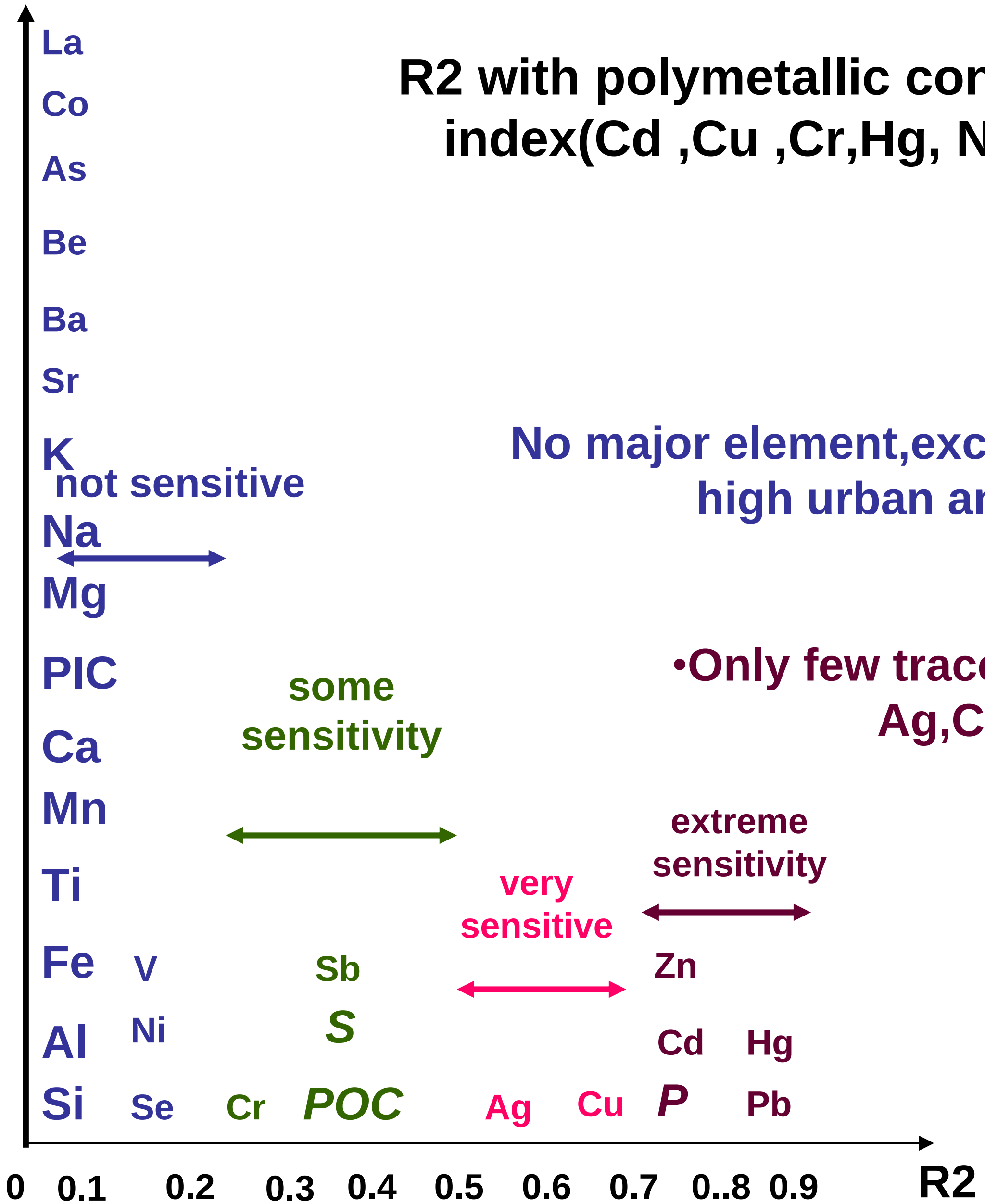
SEINE RIVER CONTAMINATIO

Zinc circulation (t/year) :1995/2000



Seine river basin contamination scale

R2 with polymetallic contamination index(Cd ,Cu ,Cr,Hg, Ni,Pb ,Zn)



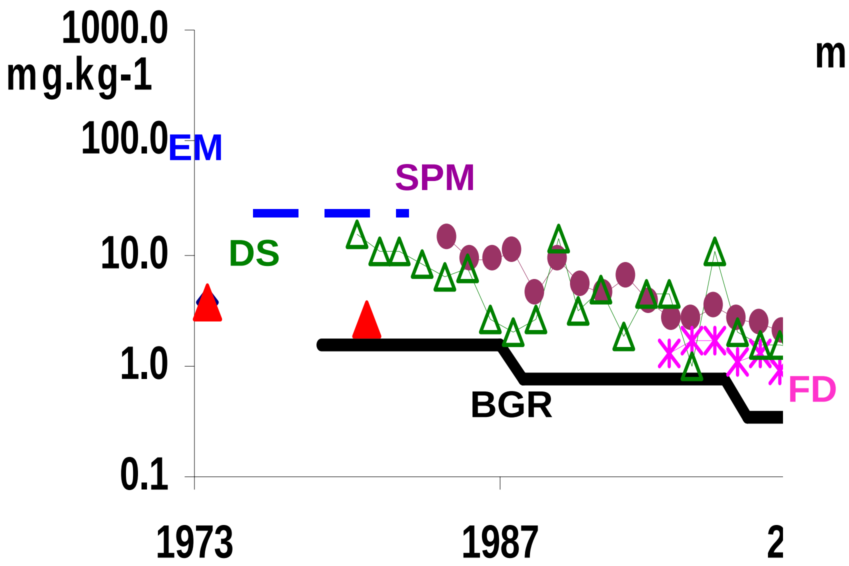
No major element,except P and POC,are sensitive to high urban and industrial pressures

- **Only few trace elements are sensitive Ag,Cu,Zn,Cd,Hg,Pb**

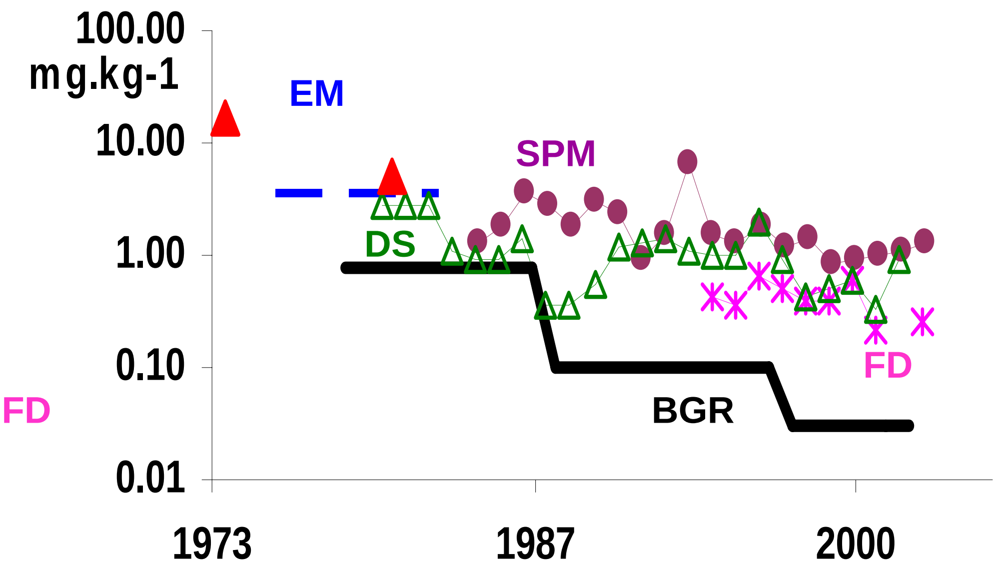
RECENT TRENDS OF METAL CONTAMINATION IN LOWER SEINE

FLOOD DEPOSITS (FD), ESTUARY SEDIMENT (EM) ,SUSPENDED SOLIDS(SPM), DEPOSITED SEDIMENTS(DS) and Background estimate(BGR) (log scale)

Cadmium

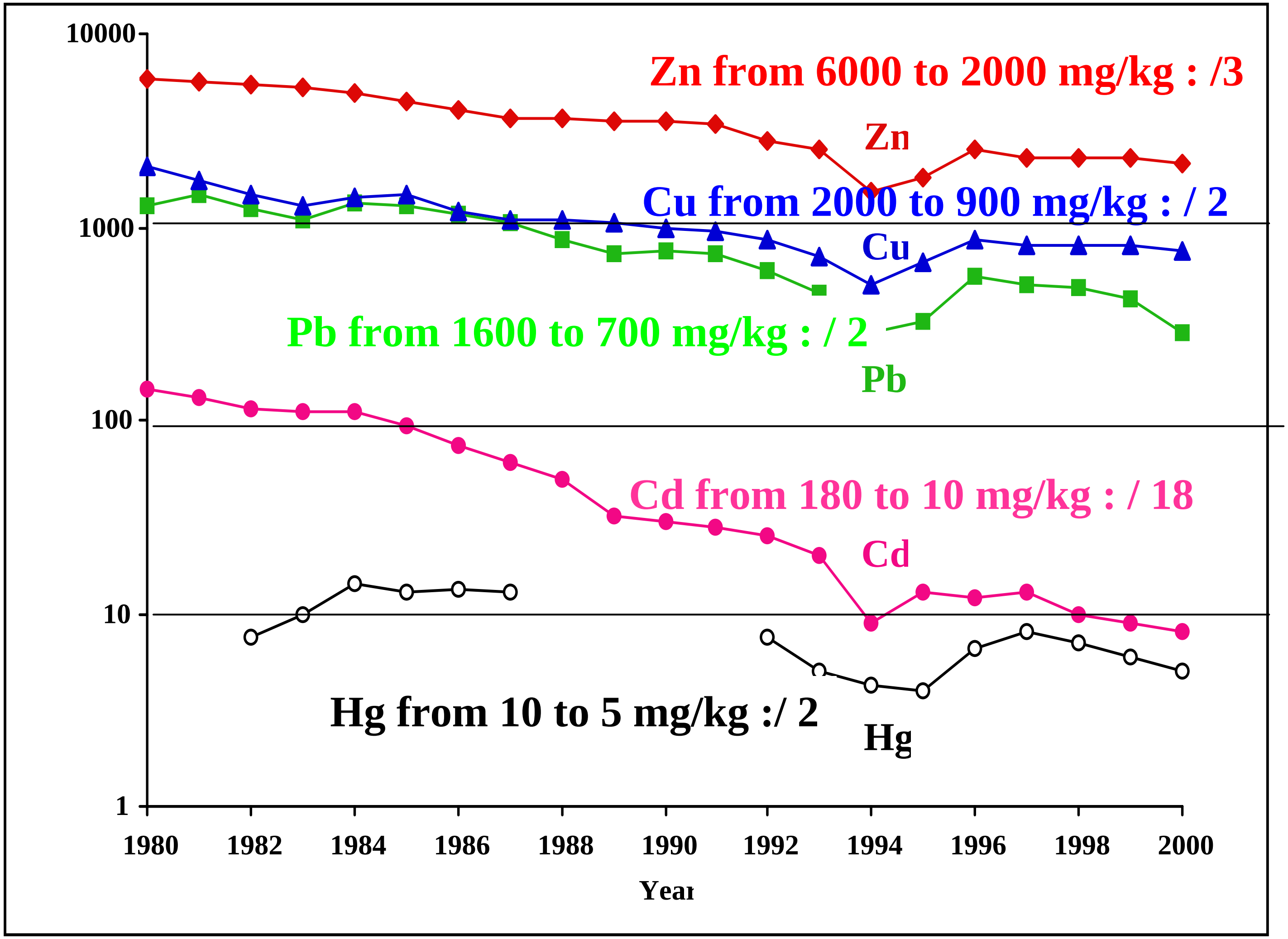


Mercury



- **Since 1973, decontamination is regular,faster for Cd than for Hg**
- **Trends are coherent on all media but SPM are generally more contaminated**
- **Background estimates have been reconsidered by scientists**

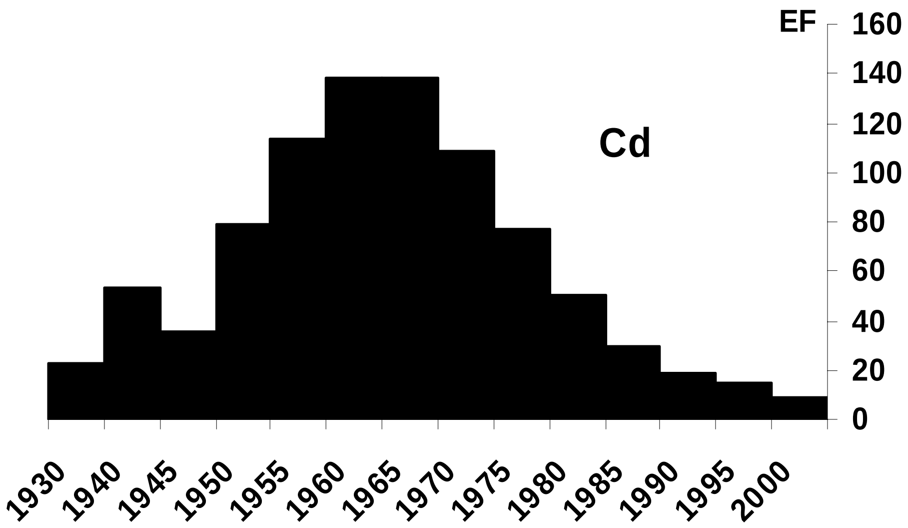
METAL CONTENTS IN SEWAGE SLUDGE (MEGA PARIS, 8Mp) 1980-2000

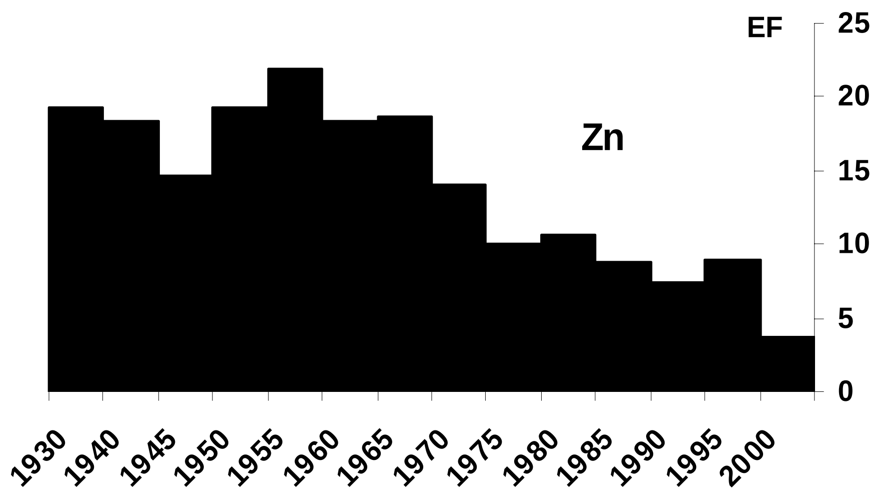


AN EXPONENTIAL DECREASE IS OBSERVED FOR ALL METALS

SEINE RIVER CONTAMINATION

Trend of Enrichment factor((Me) / (Me) basin background),from sediment archives





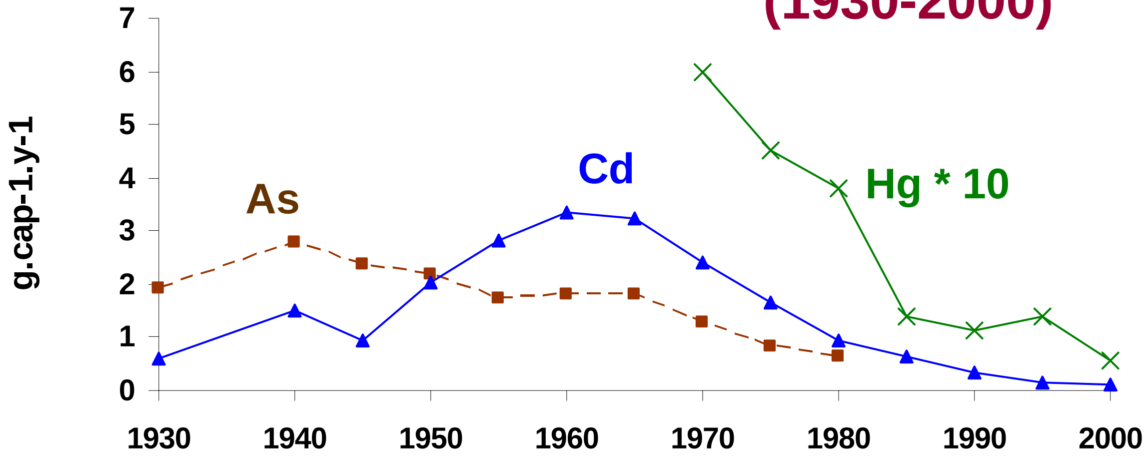
Background levels are determined on 5 000 y old sediments and on 40 subpristine forest catchments sediments

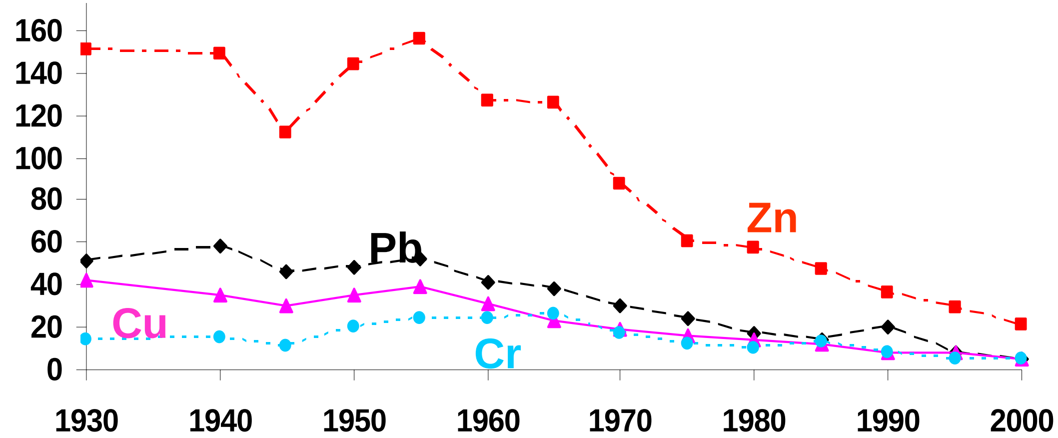
The enrichment factors are very variable:they exceed 100 times for Cd and Hg

Such extreme contamination levels are also found in other low SPM/high population density river basins in Western Europe between 1950 and 1970:Schedt, Meuse,Elbe, Rhine

SEINE RIVER CONTAMINATION

RIVER EXPORT OF EXCESS METAL PER CAPITA ($g.hab^{-1}.an^{-1}$) (1930-2000)

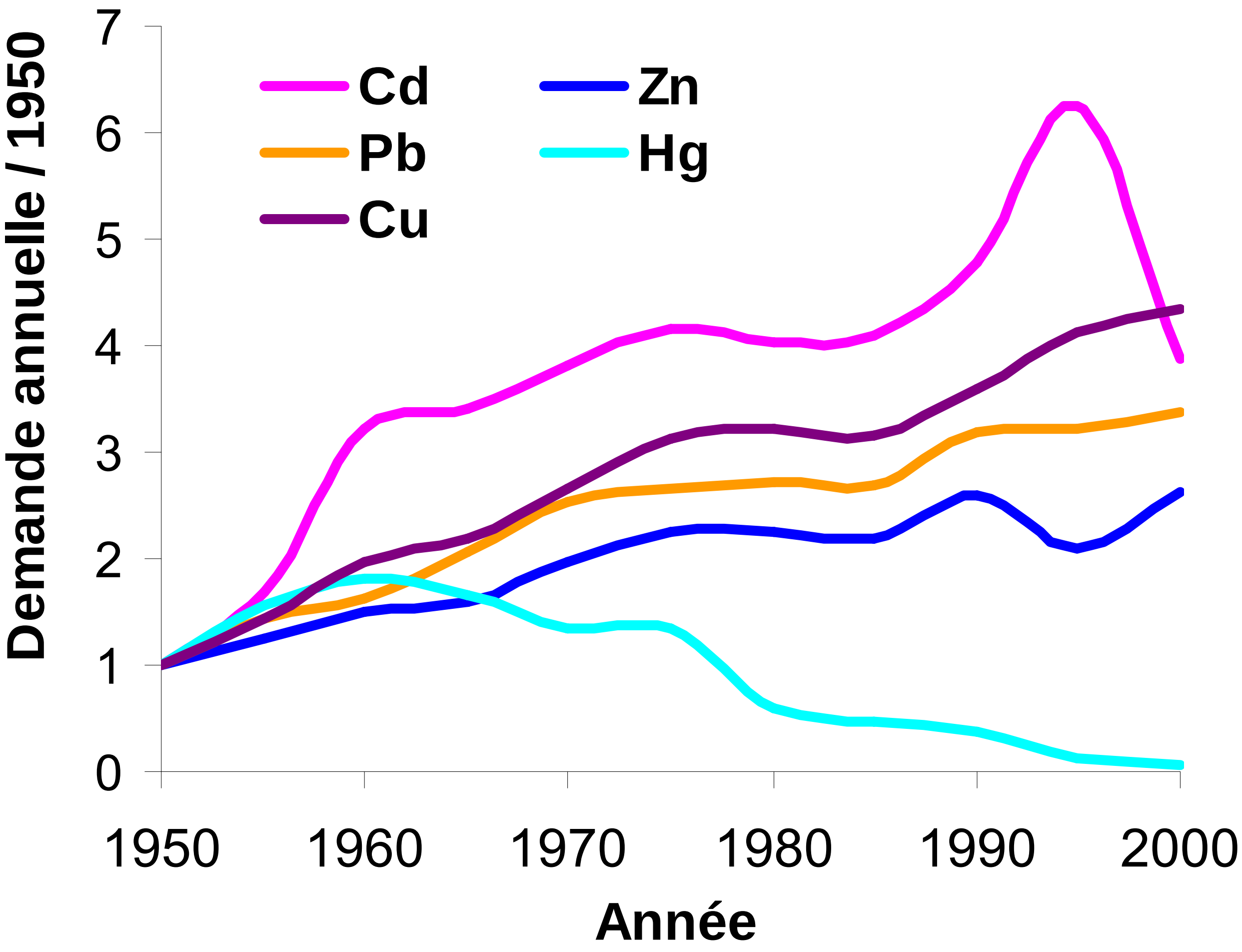




- **Per capita, leaks are very variable in time and according to metals**

- **Despite 20 % population increase, all per capita leaks are markedly decreasing, particularly in Hg since 1960, i.e. before the evidence of metal contamination**

METAL DEMAND EVOLUTION IN France (normalised to1950)



FOR Cu,Pb and Zn THE DEMAND HAS INCREASED FASTER THAN THE POPULATION.

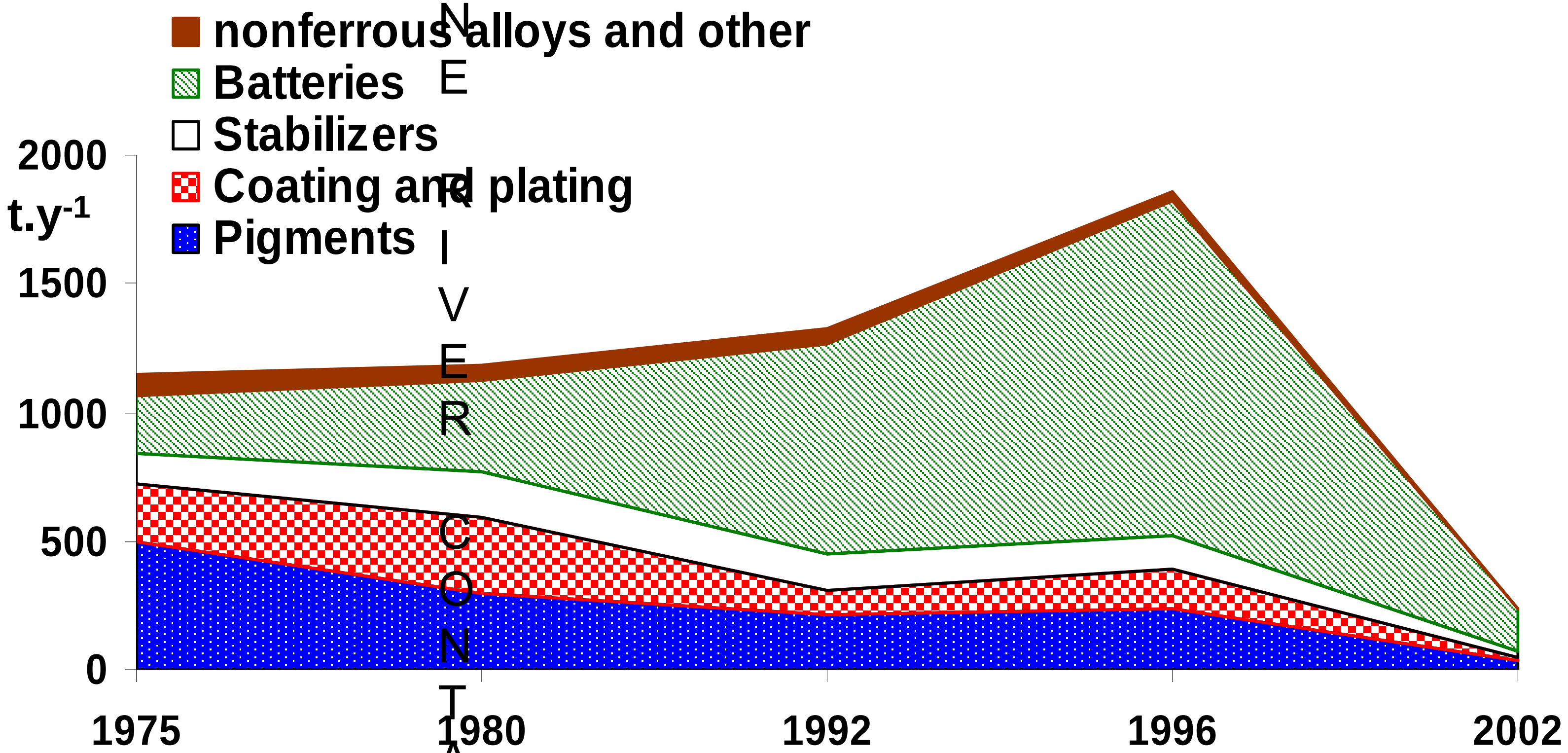
FOR Cd THE DEMAND INCREASED VERY FAST UNTILMAJOR USE LIMITATIONS IN 1995.

FOR HgTHE USE STARTED TO DROP IN 1960 THEN WAS REGULATED IN 1975

SEINE RIVER CONTAMINATION

SEINE RIVER CONTAMINATION

CADMIUM USES IN FRANCE (1975-2000)

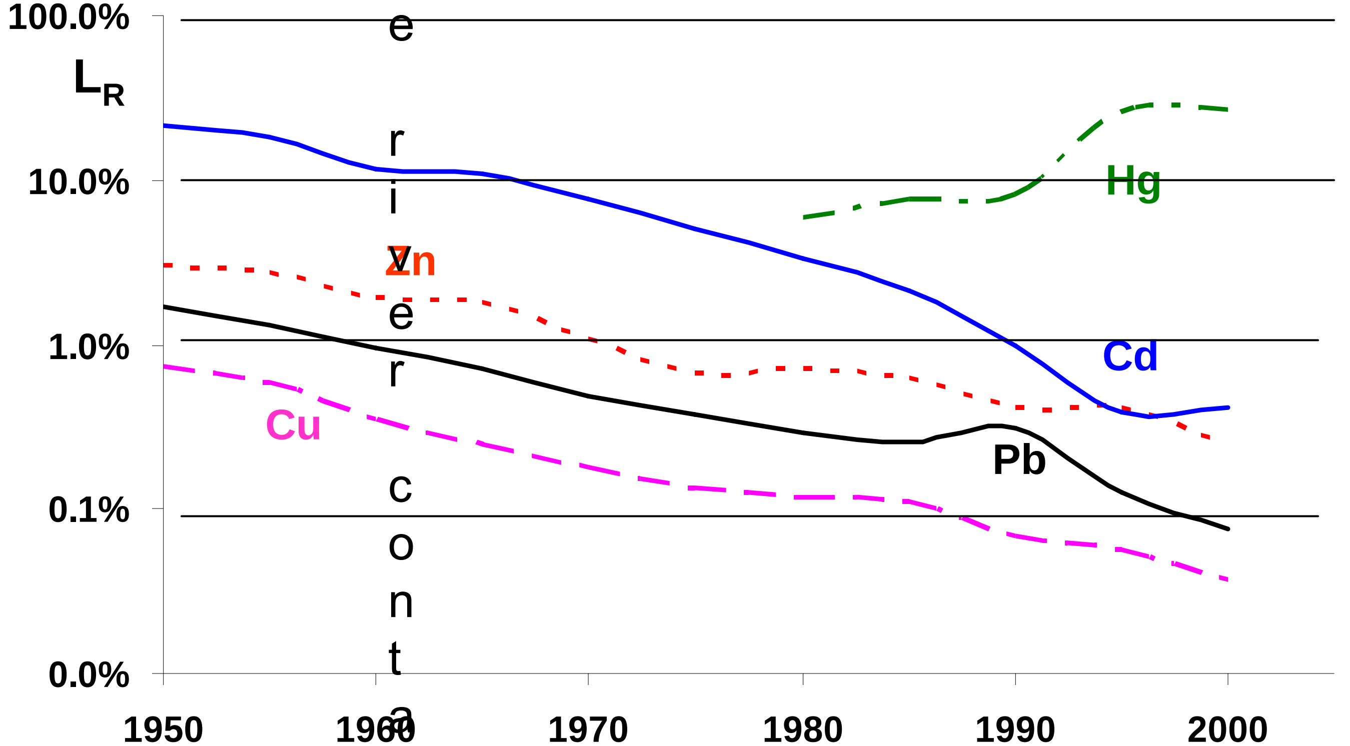


- Some industrial uses (paints, plating) have much dropped
- Cd batteries peaked in 1996 then dropped

SEINE RIVER CONTAMINATION

Seine river contamination

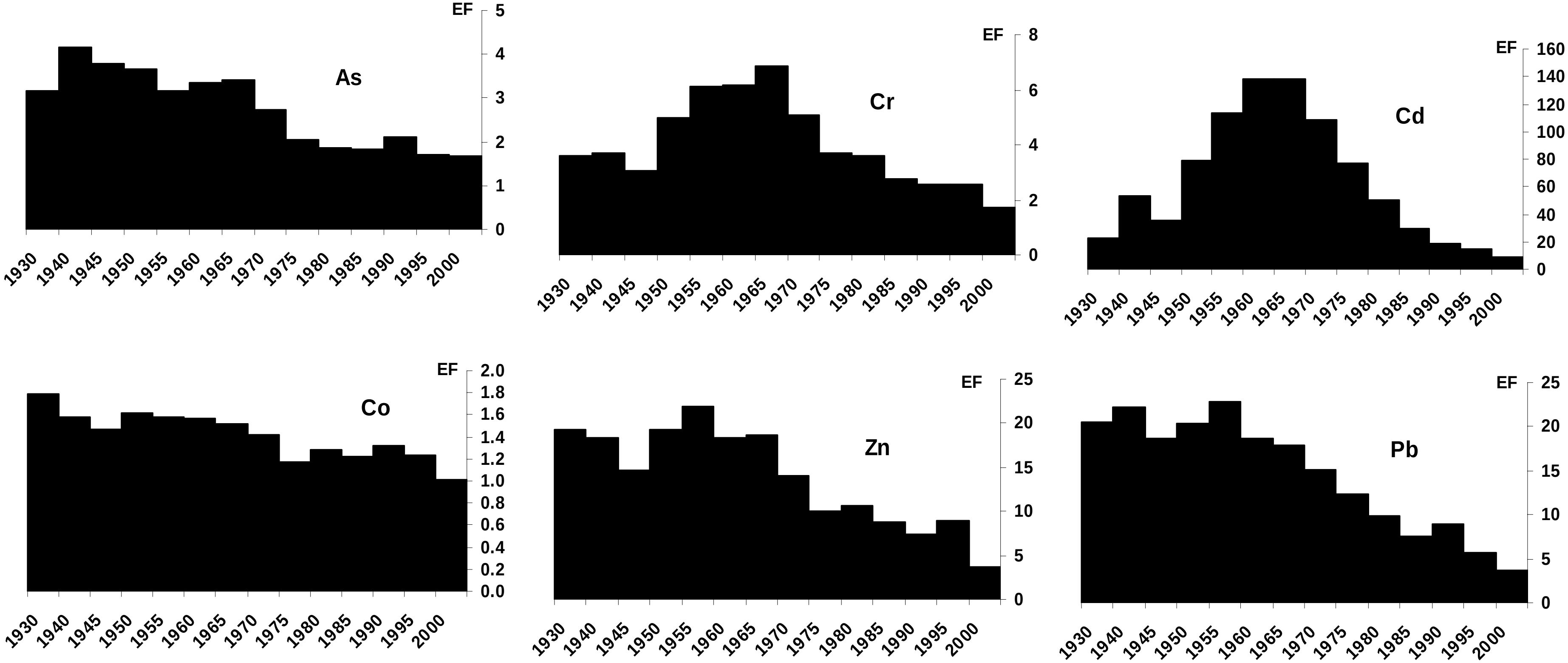
LEAKAGE RATIO OF METALS (L_R, %=demand/river excess load) 5 y averages, 1935-2000



- **Although the demand has increased from 1950 to 2000, L_R is exponentially decreasing for all metals, excepted Hg**
- **Copper: L_R from 0.8 % (1950) to 0,5‰ (2000)**
- **Hg leakage remains very high, although its demand dropped 40 times from 1960 to 2000**

SEINE RIVER CONTAMINATION

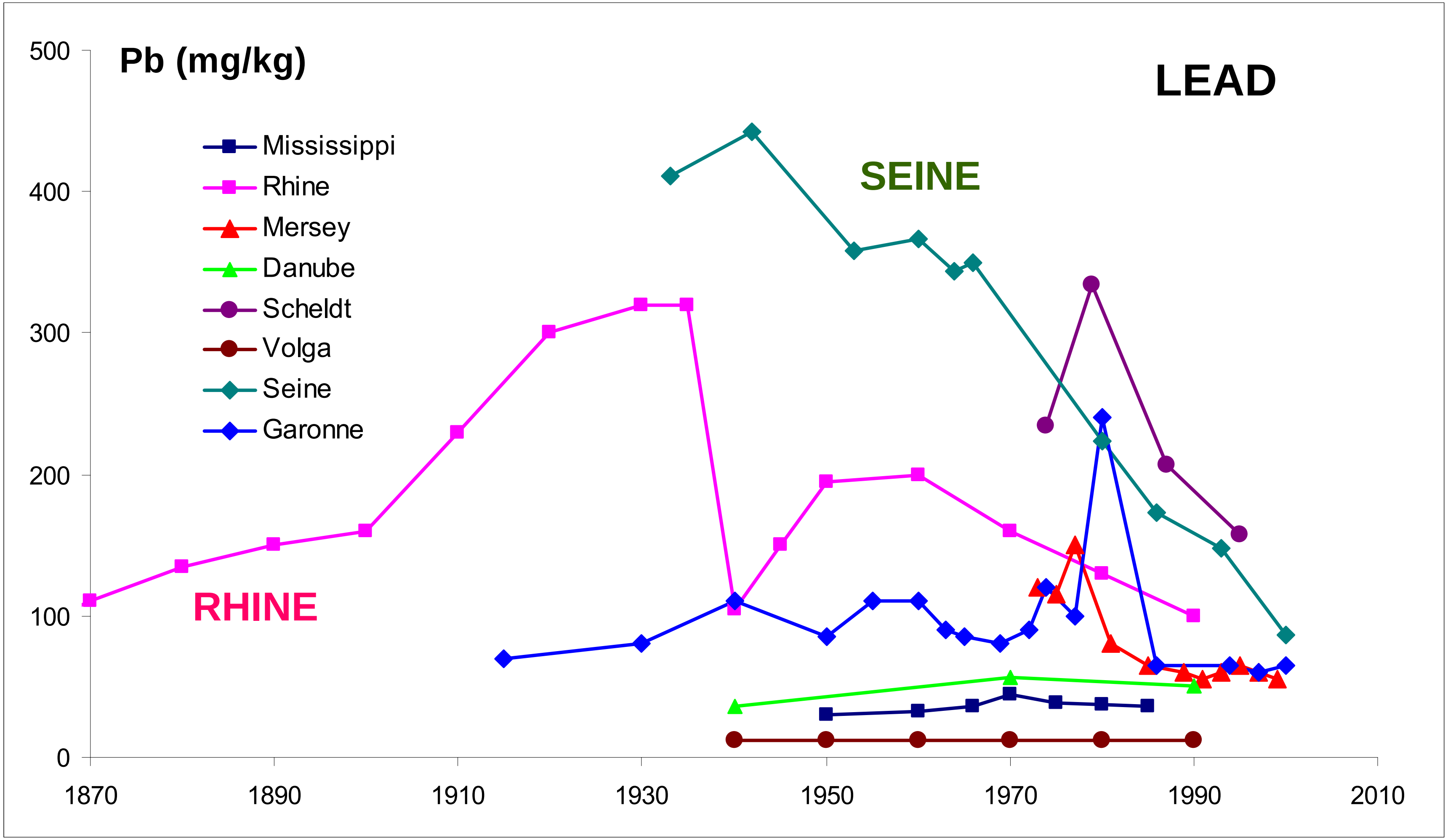
TRENDS OF METAL CONTAMINATION IN LOWER SEINE SINCE 1935 (CORES ARCHIVES) (enrichment factors)



- **Decontamination generally peaked in 1960 excepted for Co and As**
- **Since 1960, all trends show a decontamination**
- **WWII notch is marked**
- **Contamination order (maximum values) Cd = Hg ⩾ Pb = Zn > Cu = Cr = Ni > As > Co**

Meybeck et al., 2007Sci.Tot.Env.

Metal contamination trends from river flood plain sediment



- EACH BASIN HAS DIFFERENT CONTAMINATION LEVEL AND TRAJECTORY
- IN EUROPE AND N. AMERICA A DECREASE IS OBSERVED

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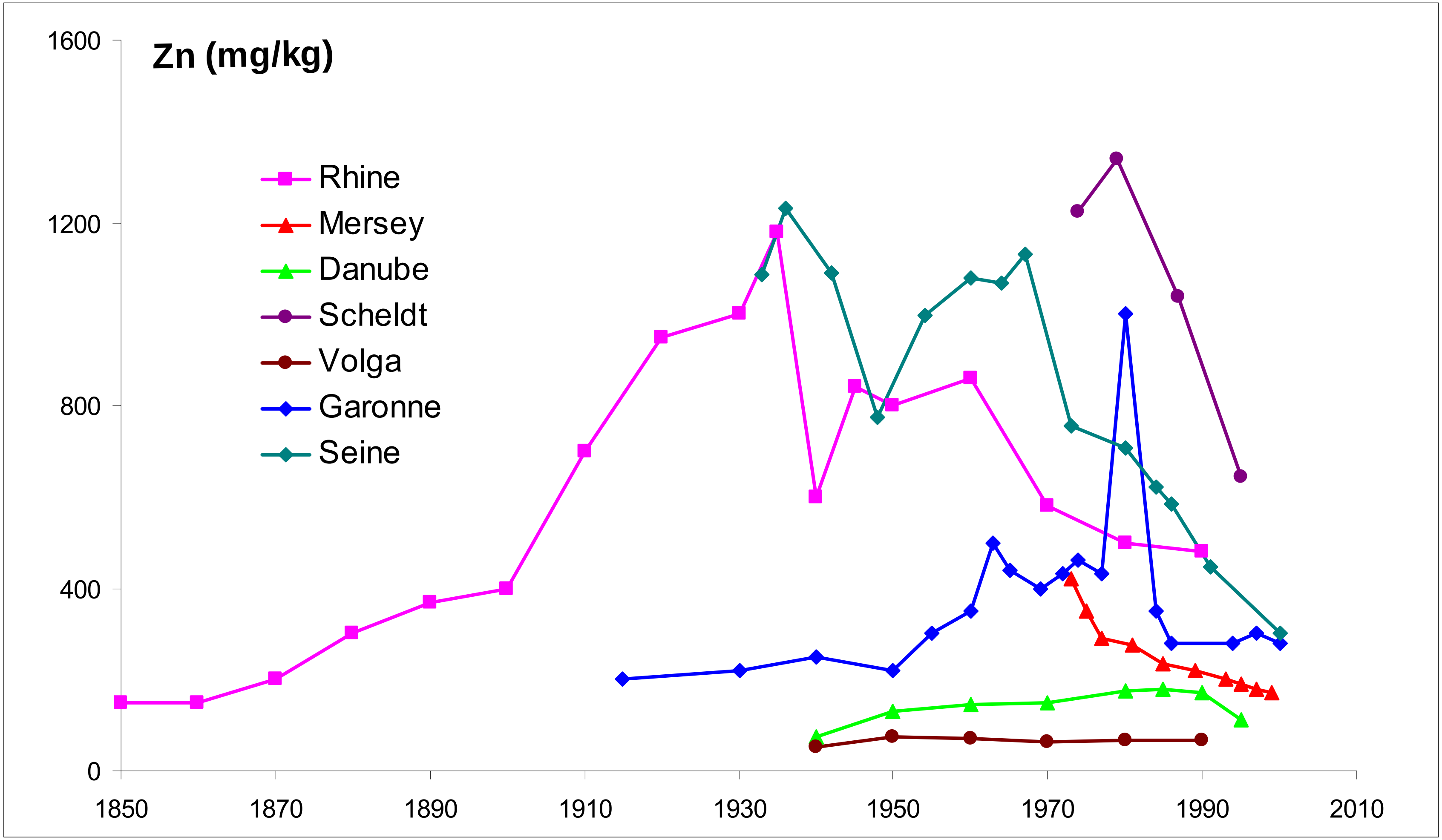
Metal contamination trends from river flood plain sediment : zinc



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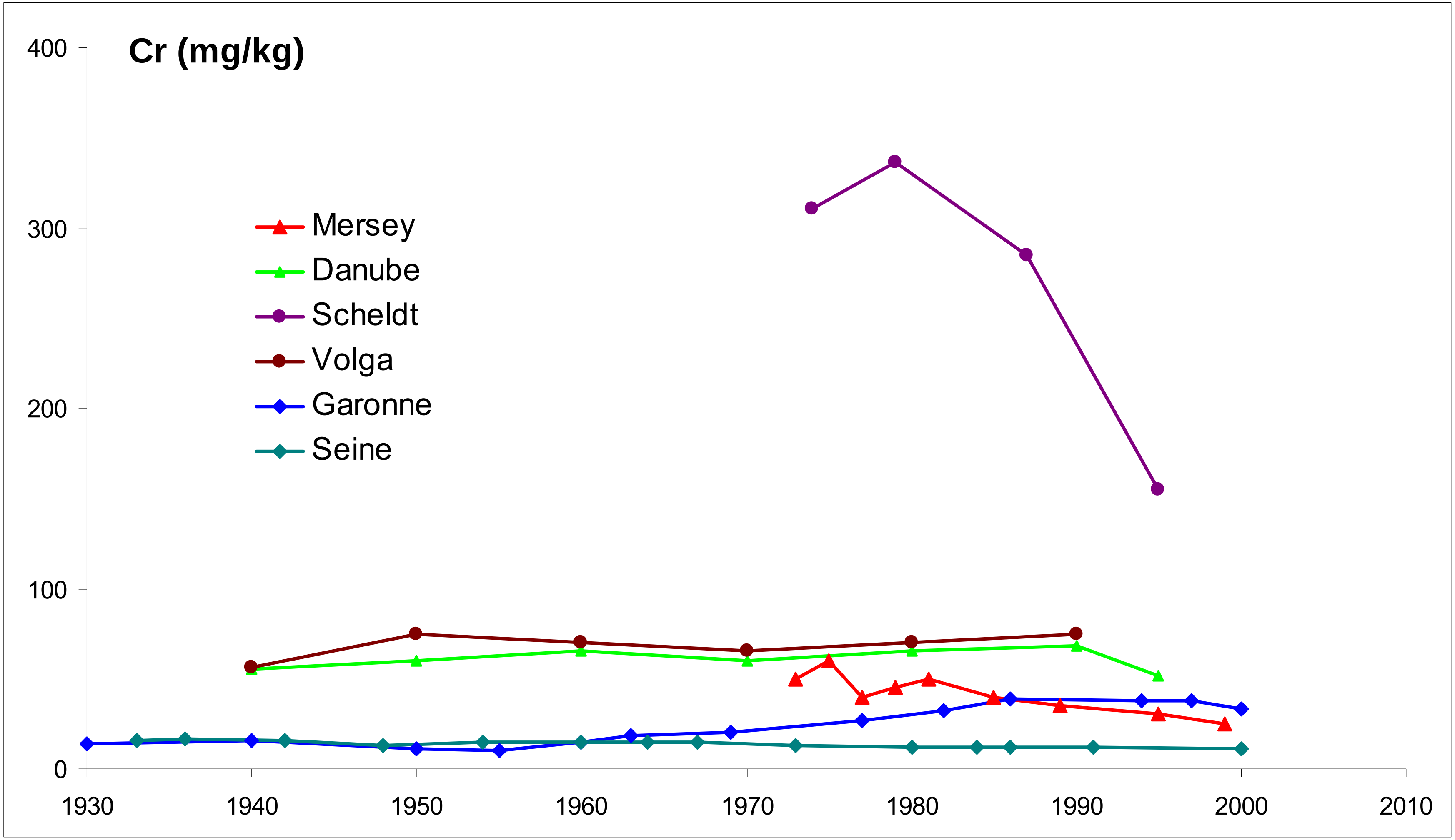
Metal contamination trends from river flood plain sediment : chromium



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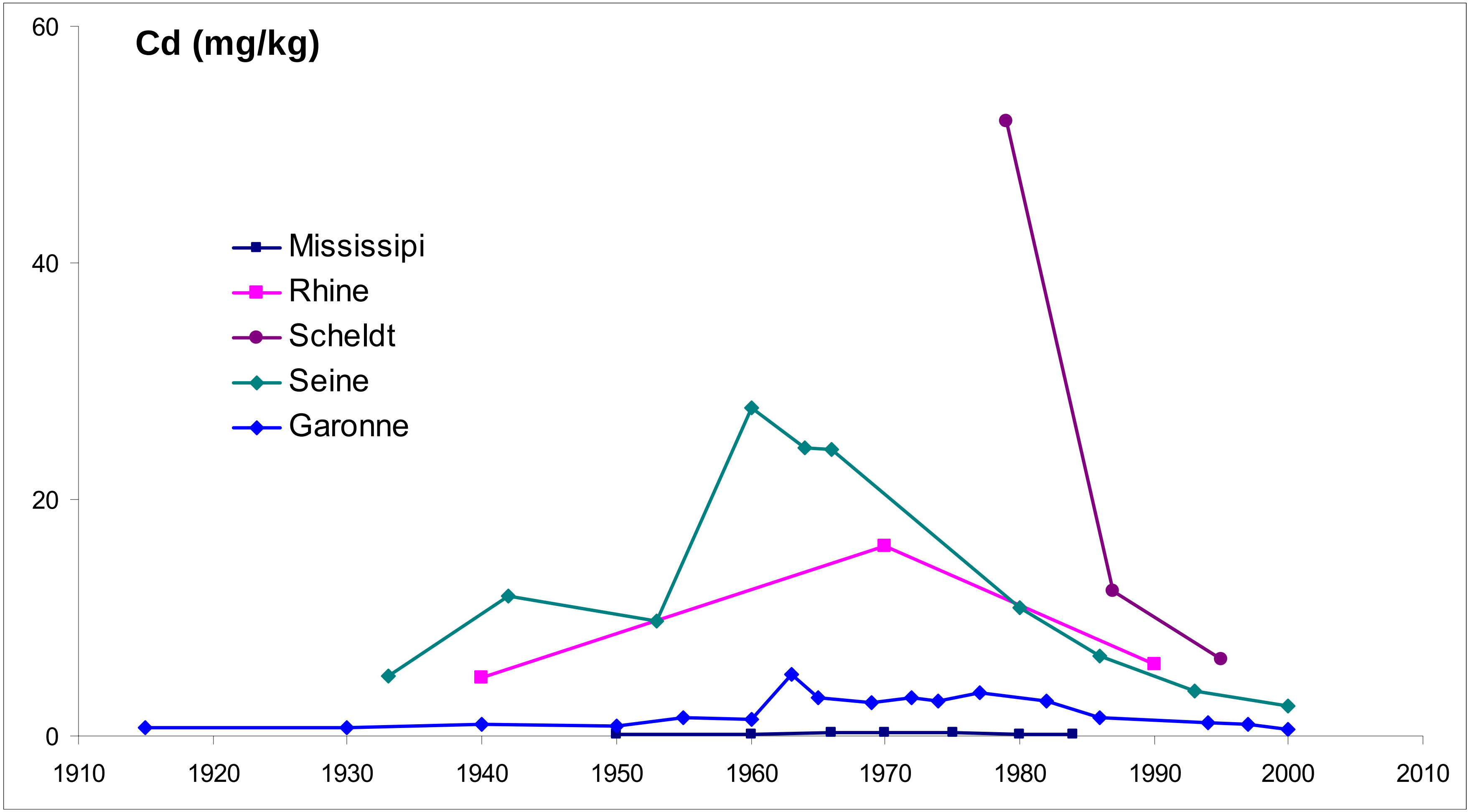
Metal contamination trends from river flood plain sediment : cadmium



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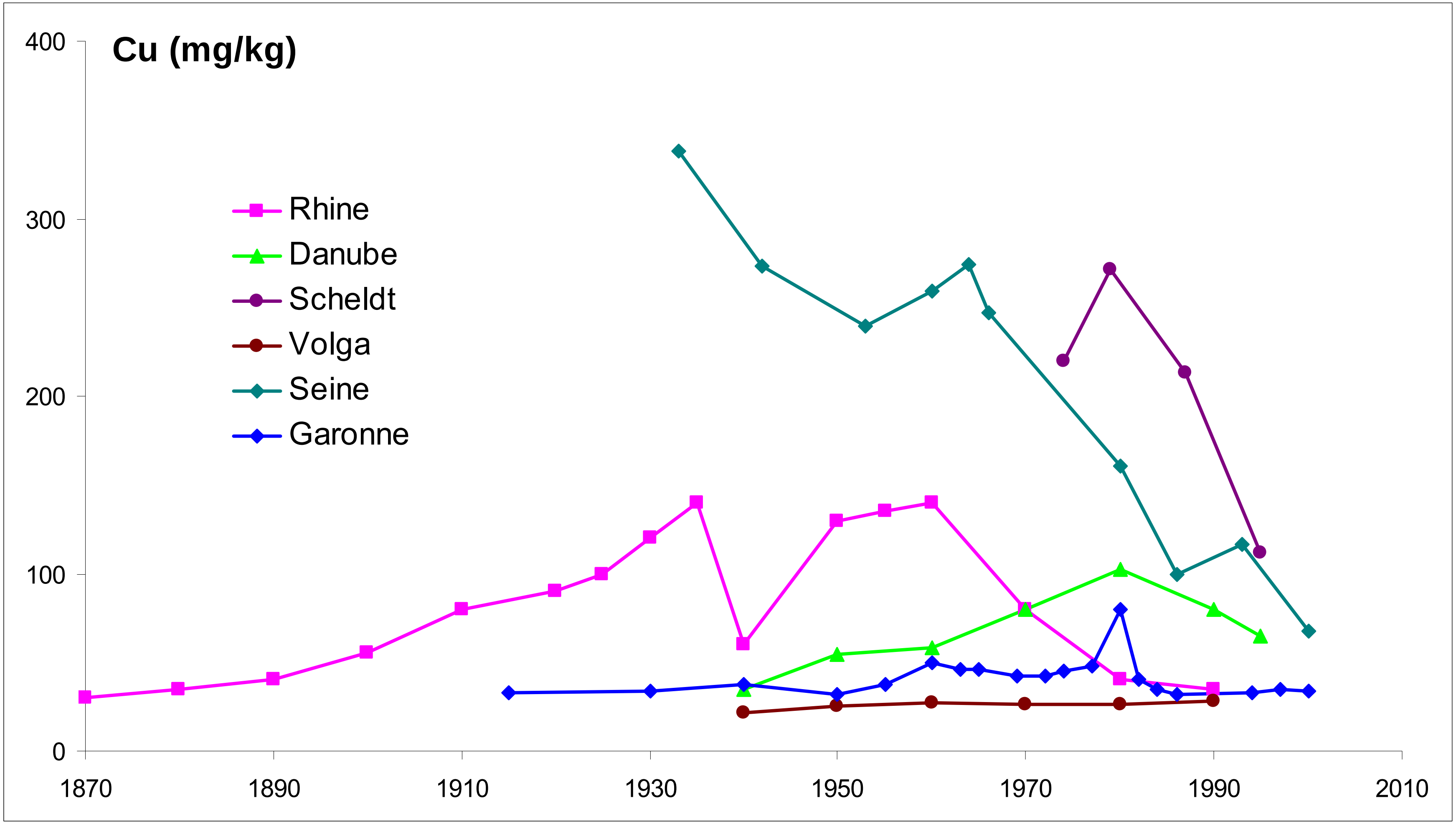
Metal contamination trends from river flood plain sediment : copper



AVERAGE RIVER METAL CONTENTS

mg/kg or ppm

	Cd	Cr	Cu	Hg	Pb	Zn
URBAN SEWER PARTICULATES average	36	440	580	2.7	105	750
HARBOURS C90	32	290	420	5	880	3100
ESTUARIES C90	7.4	400	380	1.4	480	2150
WORLD RIVERS TRIBUTARIES C90	14	230	200	2.0	255	1020
WORLD RIVERS TRIBUTARIES C50	0.5	83	39	0.12	34	120
GLOBAL RIVER MODEL	0.30	75	25	0.04	25	90

CONCLUSION

GLOBAL METAL CONTAMINATION SENSITIVITY

CONTAMINATED RIVERS(C90) vs PRISTINE RIVERS

Cd>Hg>Pb=Zn>Cu>Cr= Ni

CONTEMPORARY RIVERS (C50) vs PRISTINE RIVERS(C50)

Hg>Cd>Cu=Pb=Zn>Cr=Ni

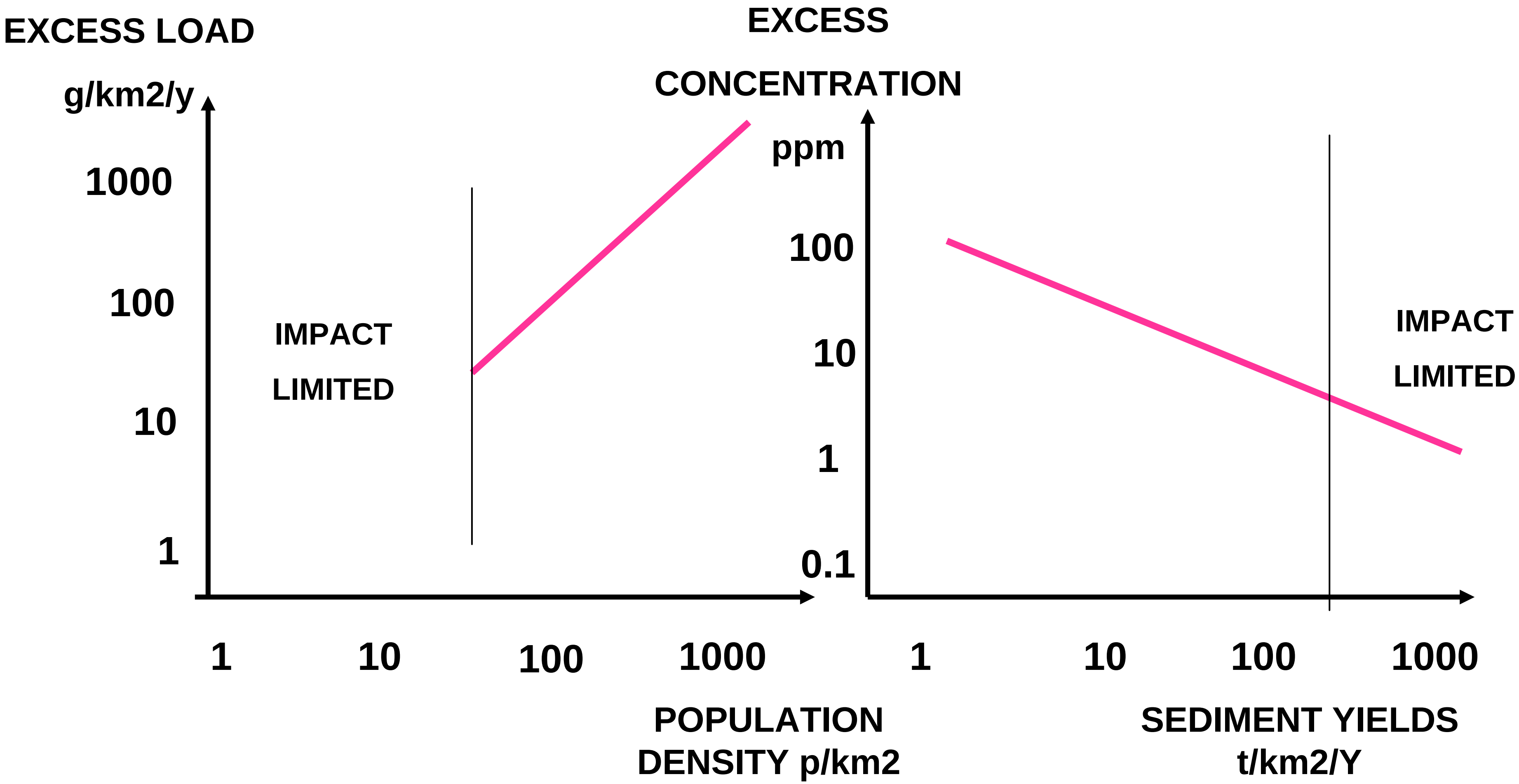
1960s FLUXES / PRISTINE FLUXES

Hg>Cd>>Zn=Pb>Cu>Cr>Ni

URBAN SEWAGE vs PRISTINE RIVER

Cd>Hg>Zn=Cu=Cr>Pb>Ni

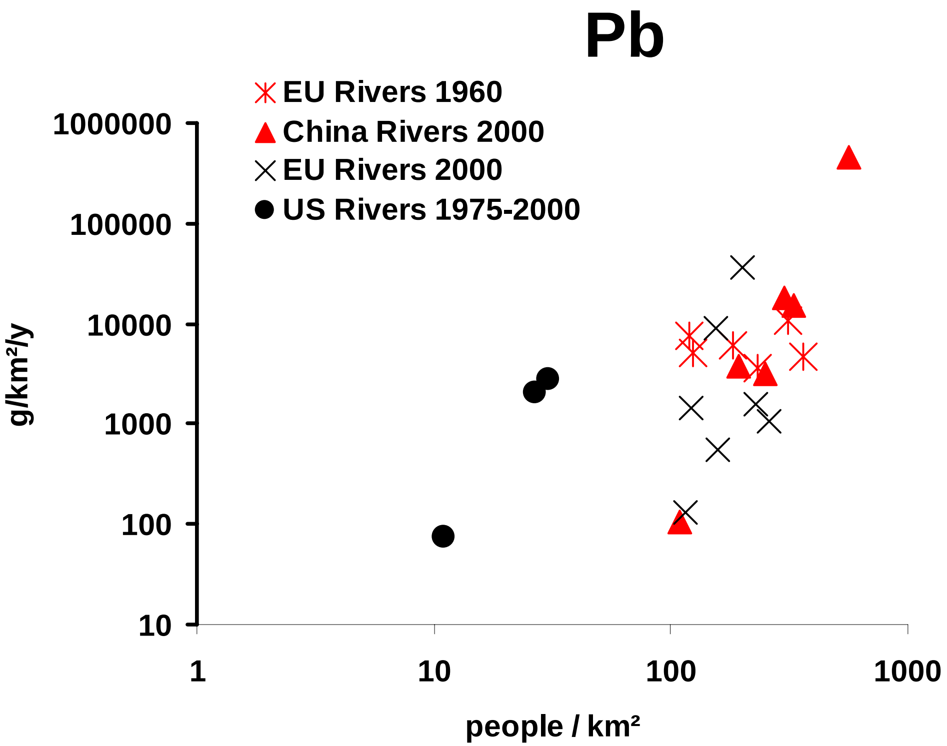
GENERAL RELATION BETWEEN PRESSURES AND CONTAMINATION

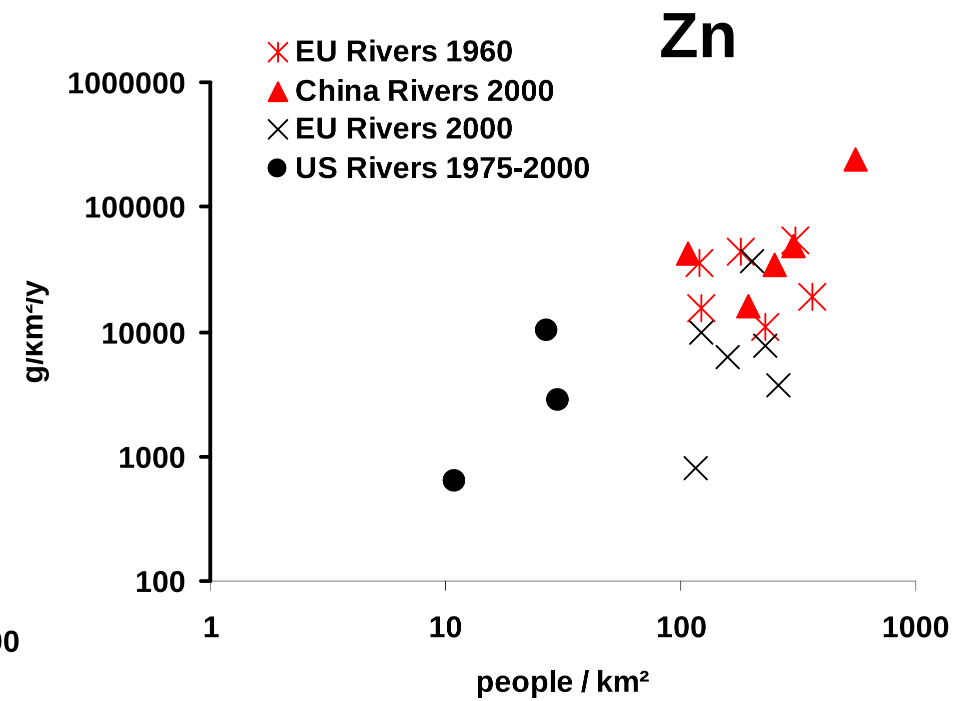


Below 20 p/km2 and above 200t/km2/y human impacts are generally limited excepted in mining areas

GENERAL METAL CONTAMINATION

EXCESS LOADS (g/km2/y) vs POPULATION DENSITY

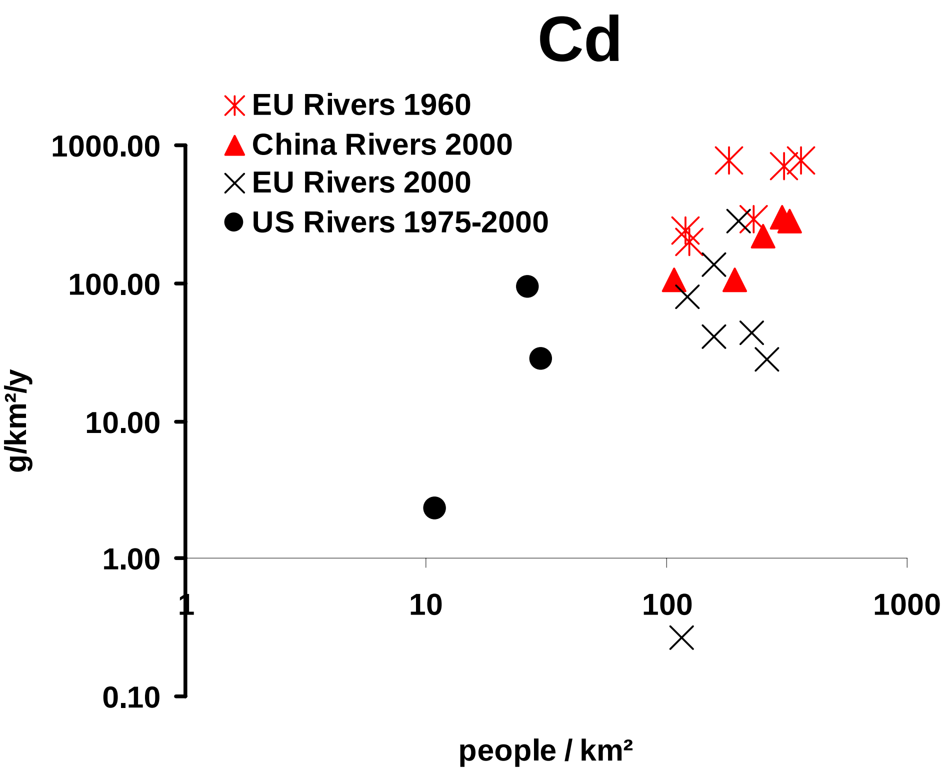


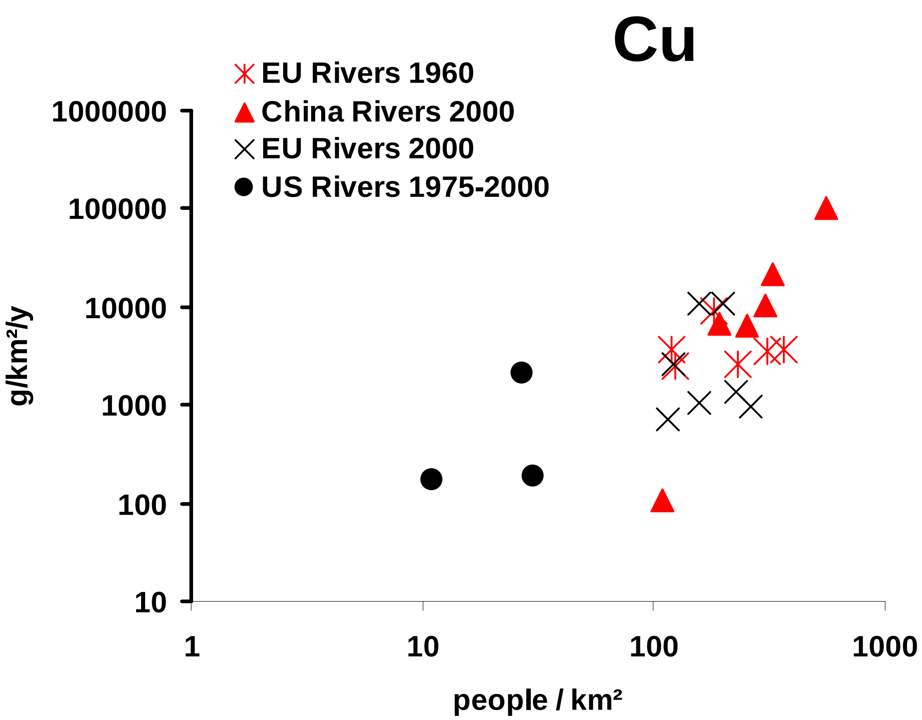


- POPULATION IS THE#1 FACTOR OF SPECIFIC EXCESS LOADS
- TRENDS ARE NOTED
- CHINA AND US LOADS ARE MORE UNCERTAIN THAN EUROPE’s

GENERAL METAL CONTAMINATION

EXCESS LOADS(g/km2/y) vs POPULATION DENSITY





GLOBAL METAL CONTAMINATION MODEL

PER CAPITA LOADS g/cap/y

	Cd	Cr	Cu	Hg	Pb	Zn
EUROPE RIVERS 1960s	2.8	64	31	0.75	34	175
EUROPE RIVERS 2000s	0.5	18	20	0.10	22	63
Clean cities urban sewage 2000(*)	0.07	3	7	0.05	2	14
Rural Seine, Streams 2000	0.055		3.6	0.025	4	14

(*) Stockholm, Montreal ,Paris ,2000s

GLOBAL RIVER CONTAMINATION MODEL

- **STEP 1:TYPOLOLOGY OF PER CAPITA INPUTS TO RIVERS**;
- 8 EUROPEAN RIVERS(2 US RIVERS,6CHINA RIVERS)
- CITY BUDGETS:STOCKHOLM,PARIS,MONTREAL
- RURAL POPULATION BUDGET(SEINE BASIN)
- **STEP 2 SCENARIOS OF RELATED WORLD POPULATION(Mpeople)**

	1960	2000 LOW	2000 HIGH	TYPOLOGY
DURTY INDUSTRIAL	1200	200	1000	EU 1960
MID DURTY INDUS	0	900	500	EU 1960 x 0.5
CLEANER INDUSTRIAL	0	1000	1000	EU 2000
DEVELOPED RURAL	500	2000	1500	SEINE RURAL
MID DEV; RURAL	500	1000	1100	SEINE RURAL X0.5

- **STEP 3:population x per capita loads**

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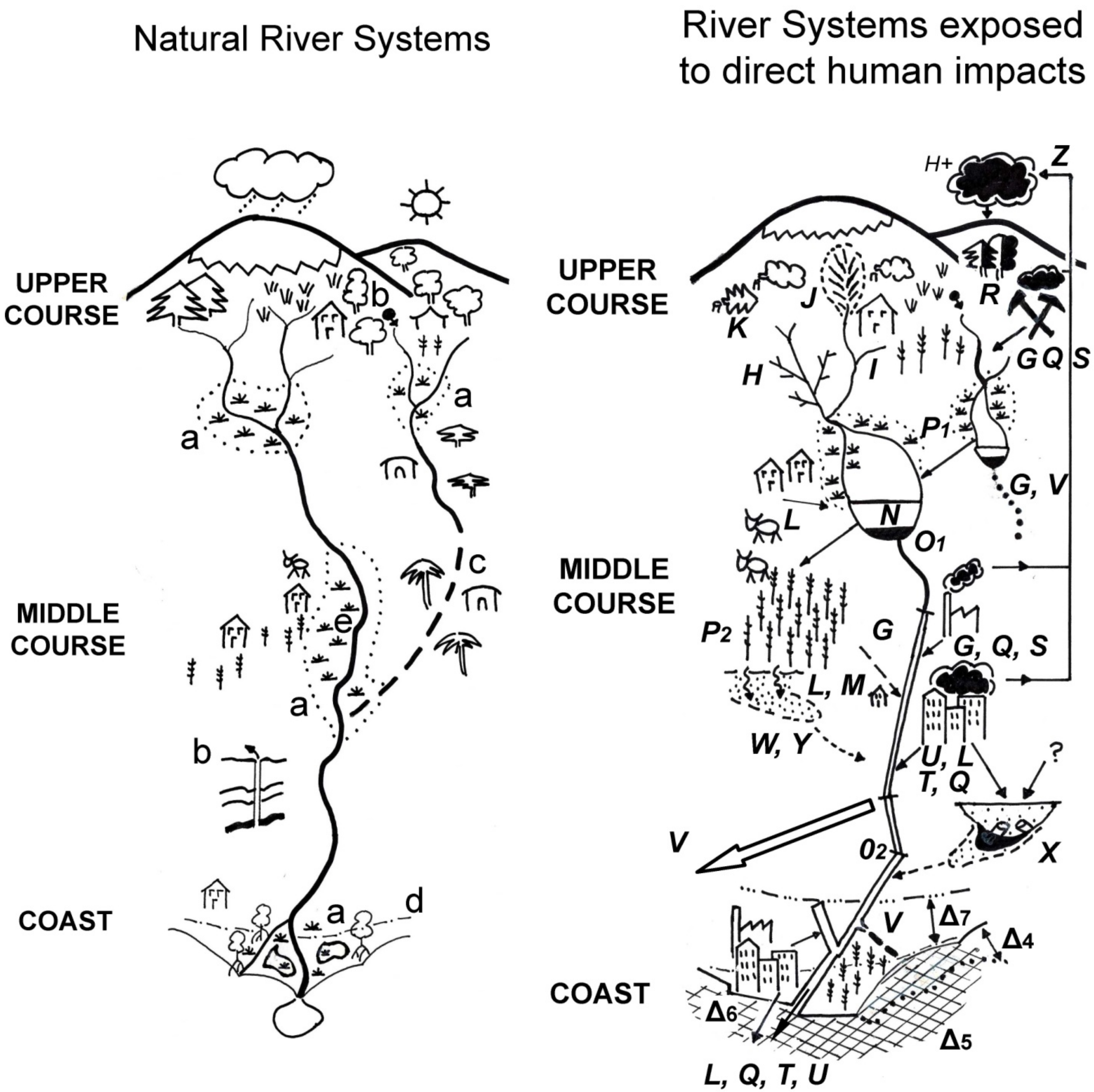
GLOBAL RIVER CONTAMINATION MODEL

EXCESS RIVERS LOADS (t/y)

	Cd	Hg	Pb	Zn
1960s	3400	900	44000	220 000
TOTAL/NATURAL	1.6	2.1	1.10	1.1
2000 LOW	2500	650	54000	210 000
TOTAL/NATURAL	1.4	1.8	1.1	1.1
2000 HIGH	4150	1080	72000	300 000
TOTAL/NATURAL	1.7	2.35	1.15	1.15
NATURAL LOADS	6000	800	500000	1 800 000

DIRECT IMPACTS ON METAL FLUXES IN RIVER BASINS



METAL
SOURCE SINK

DEFORESTATION +

MINING +++

ACID RAIN +

CLIMATE CHANGE +

RESERVOIR - - -

INTENSIVE AGRICULTURE +

WETLAND DRAINING

WATER DIVERSION -

WATER LOSS FROM IRRIGATION

INDUSTRIAL WASTES +++

URBAN WASTES +++

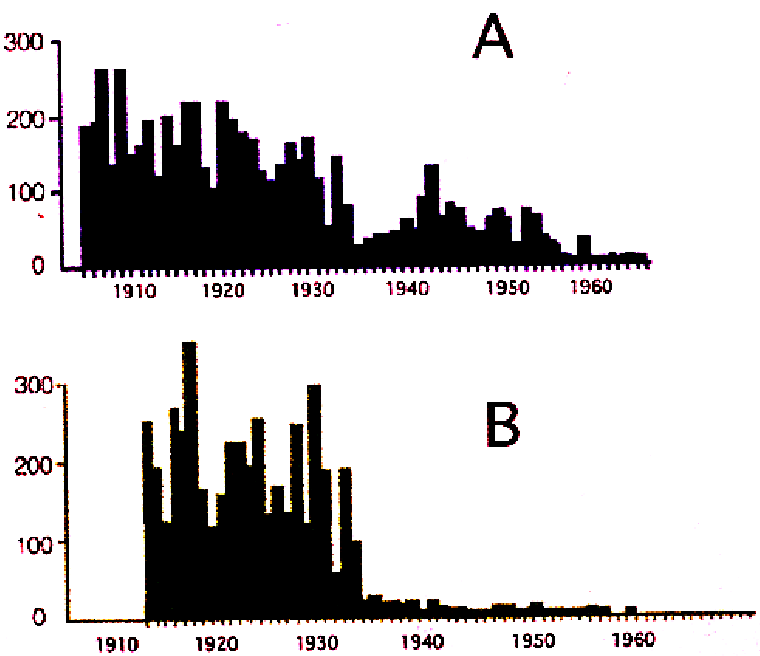
DREDGING - -

CHANNELISATION

SEDIMENT STARVING - - -

RIVER FLUXES TRENDS AFTER DAMMING THE COLORADO EXAMPLE (1910-1960)

Colorado (USA)
Trend in water discharge (A) and sediment discharge (B) after damming (1936)
(Meade and Parker, 1985)



A : annual water flow

B : annual sediment flux

- Colorado changes are some of the most dramatic change documented in a river system
- This evolution was triggered by the construction of the Hoover Dam in 1936

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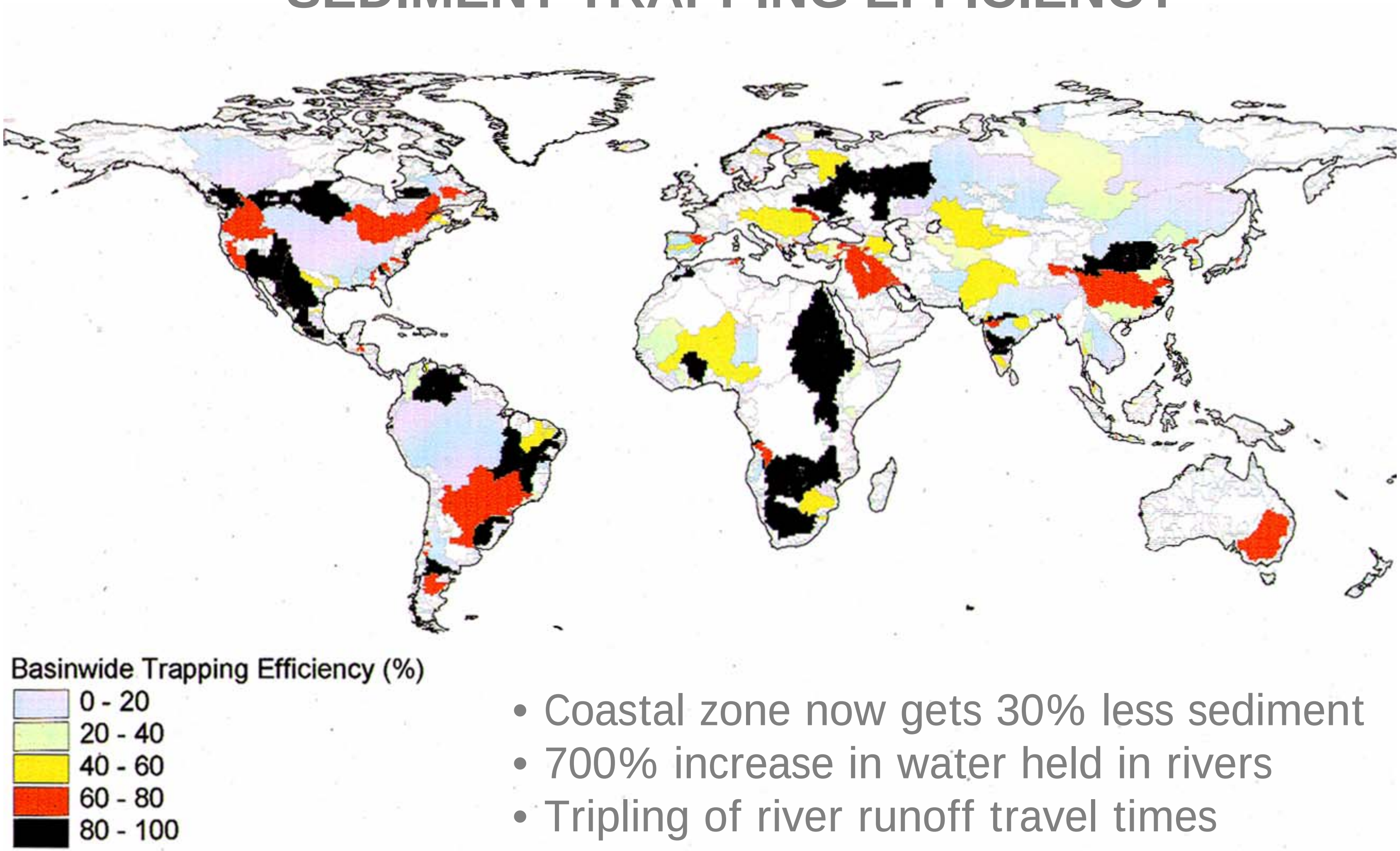
GLOBAL IMPACT OF LARGE RESERVOIRS : SEDIMENT TRAPPING EFFICIENCY



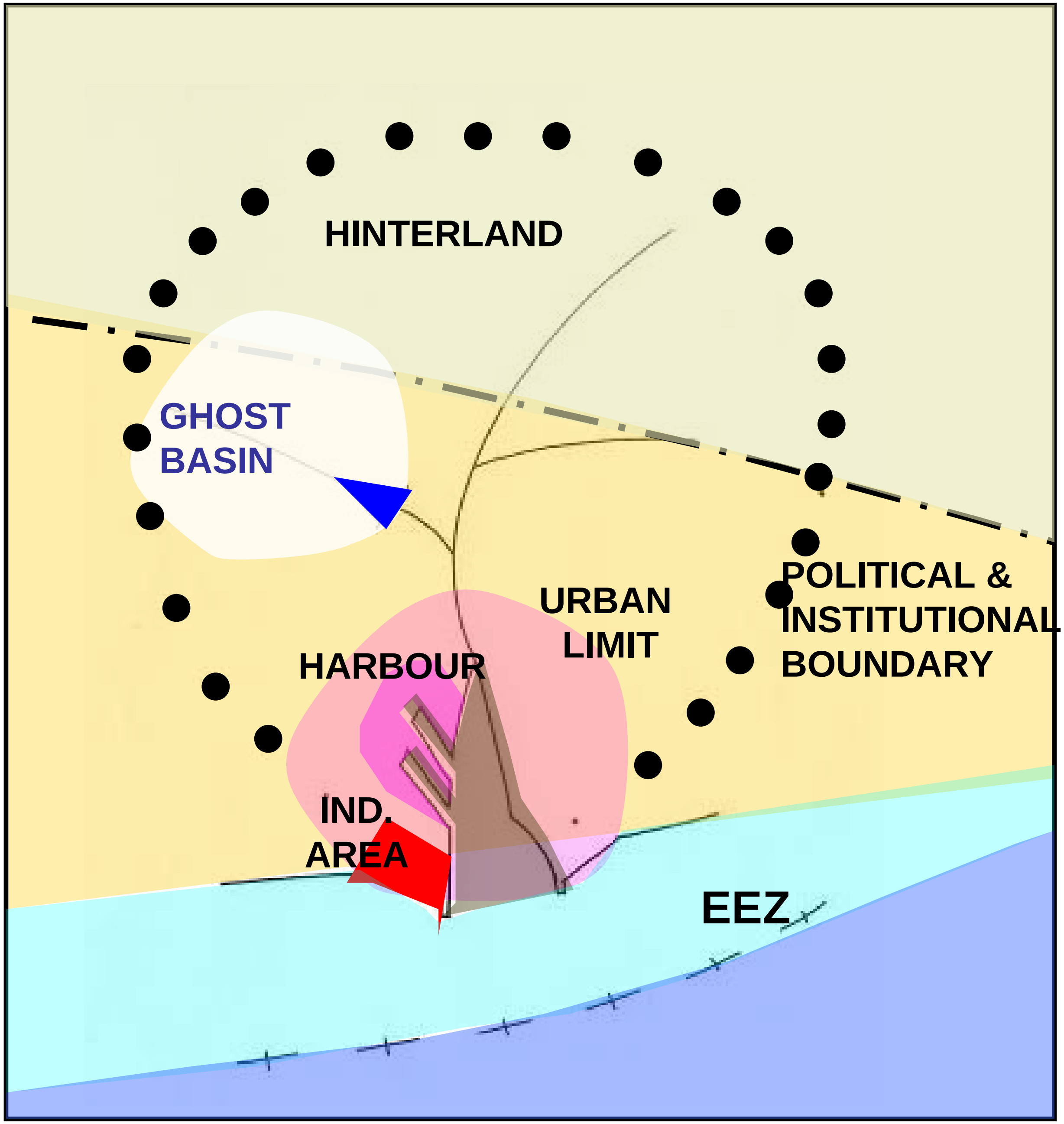
- Coastal zone now gets 30% less sediment
- 700% increase in water held in rivers
- Tripling of river runoff travel times

Sediment starving is a growing issue in some coastal zone

UNH

Vörösmarty et al. 2003

Topology of impacted river basin/estuarine system



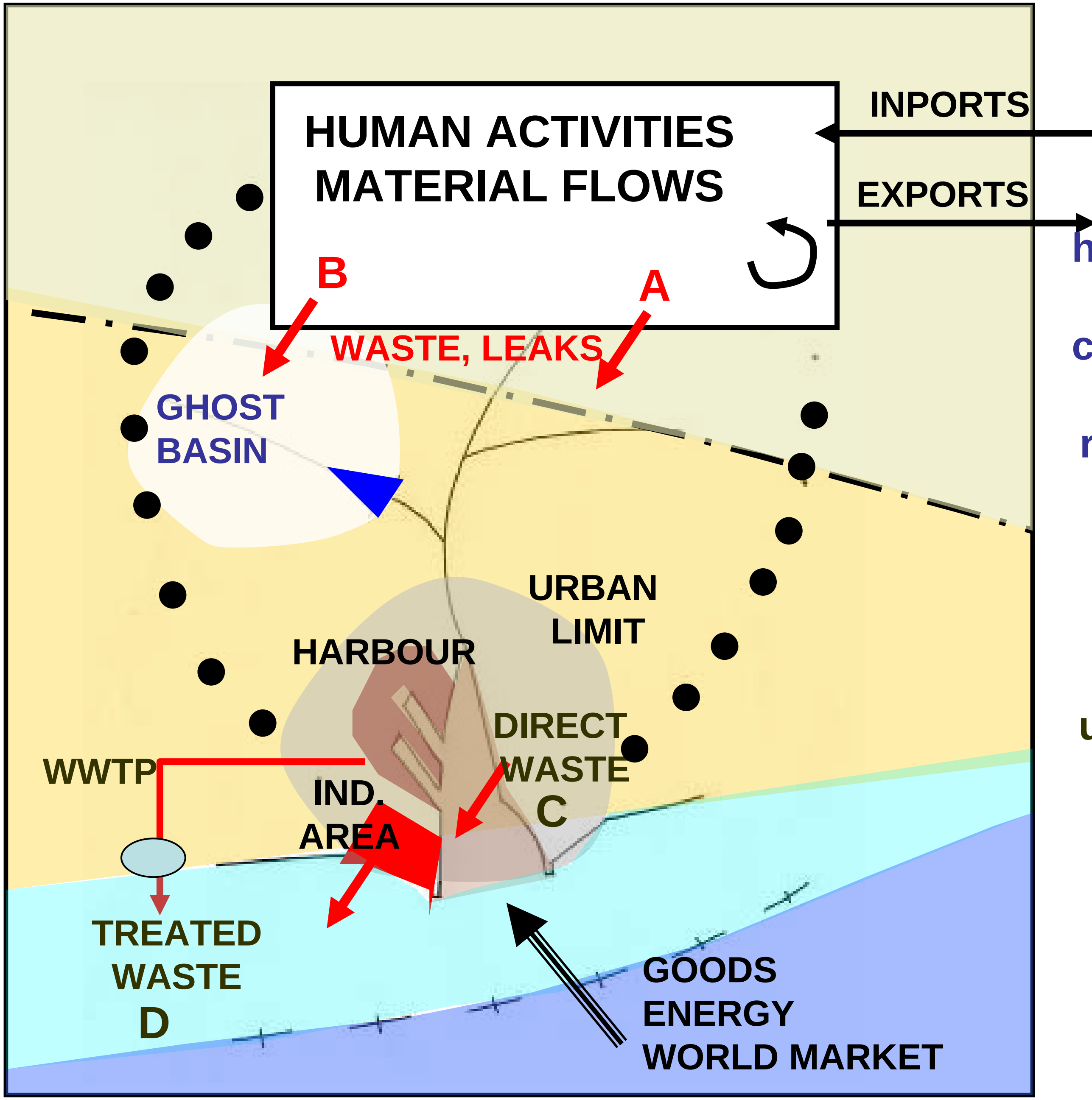
(HUMAN DIMENSION)

- Basin boundaries are often masked
- by political/institutional limits

- Estuarine limits may be hidden by urban growth

- Part of river basins may be intercepted by reservoirs
- Other limits can be defined in the coastal zone

Topology of impacted river basin/estuarine system



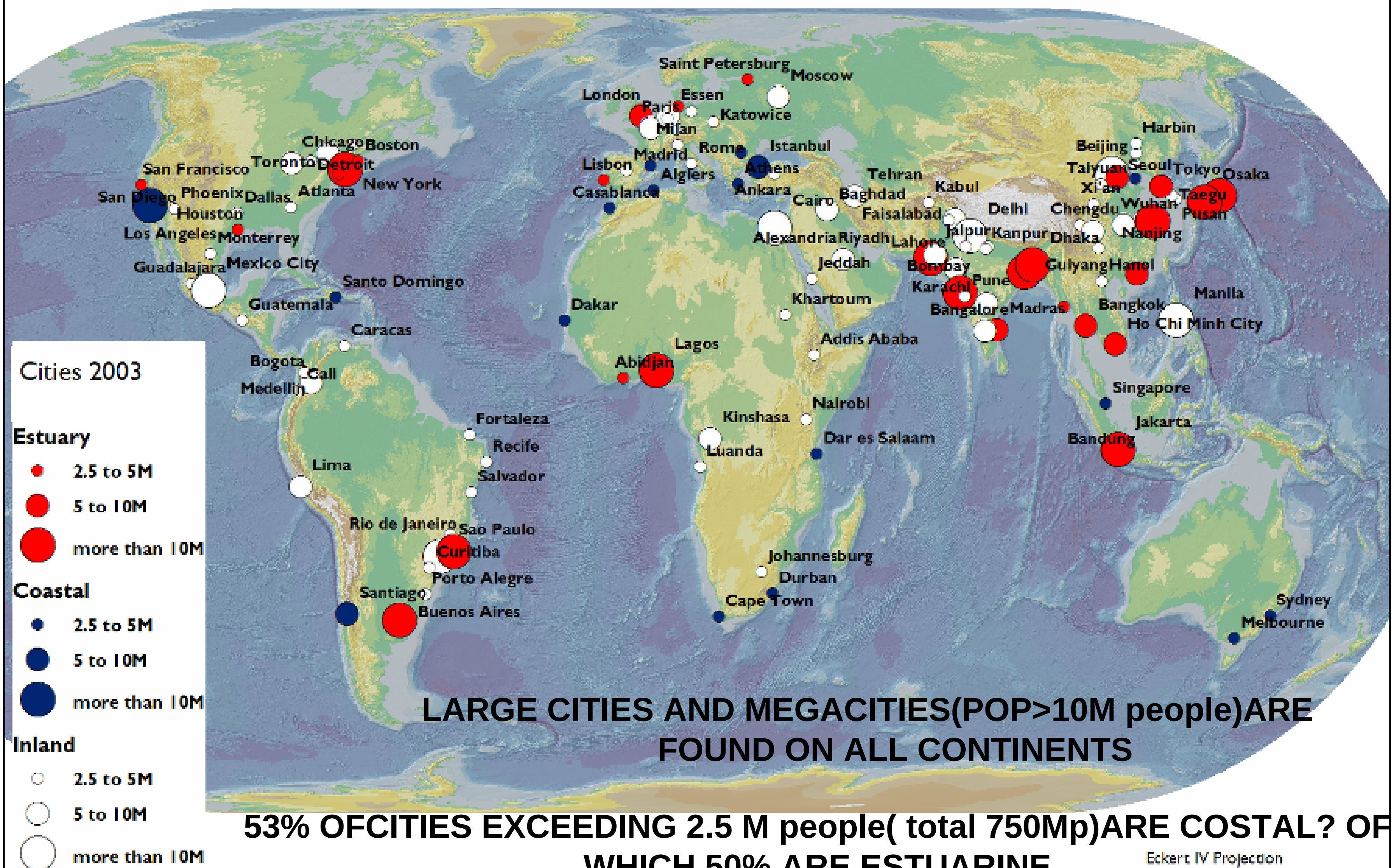
(HUMAN DIMENSION)

- Within the river basin human activities generate extra fluxes to river courses(wastes, leaks)(A)
- And extra sinks (e.g. reservoirs) that trap river material(B)

- Estuarine reactors and filter capacities are greatly modified by land use, dredging,reclamation

- Direct untreated wastes(C)and treated wastes from urban ,industrial and harbour sources(D) are difficult to assess

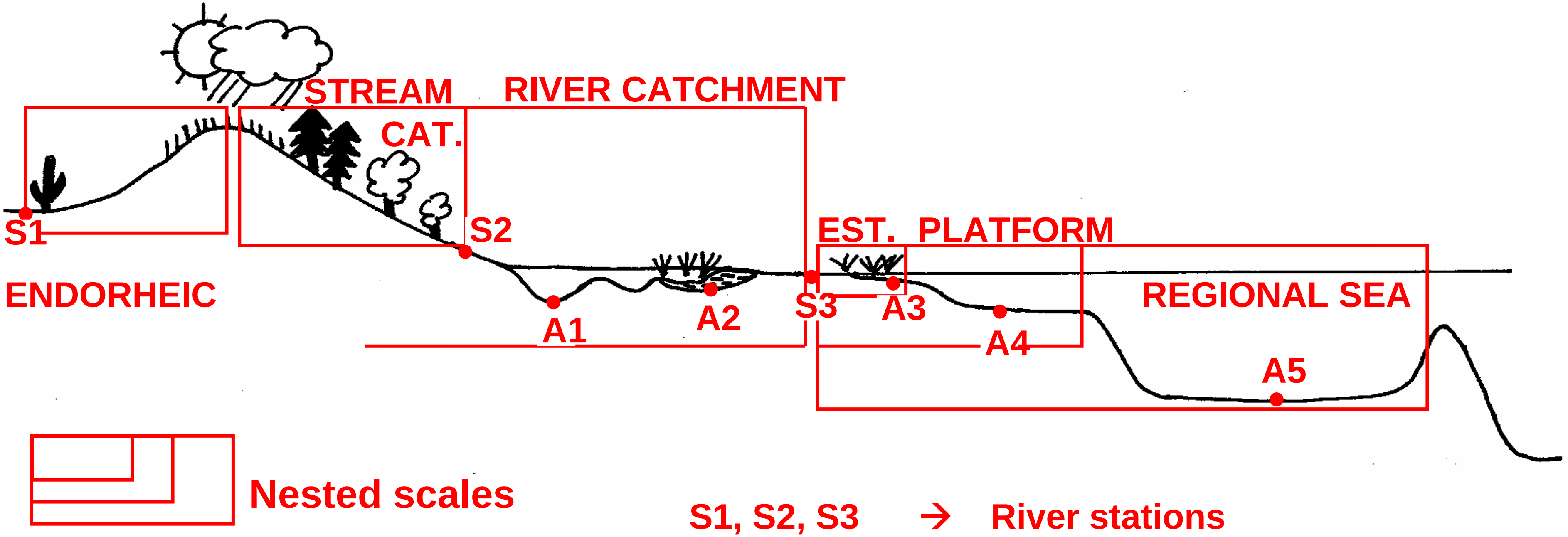
Location of biggest cities of the world (2003)



LARGE CITIES AND MEGACITIES(POP>10M people)ARE FOUND ON ALL CONTINENTS

53% OFCITIES EXCEEDING 2.5 M people(total 750Mp)ARE COSTAL? OF WHICH 50% ARE ESTUARINE

Nested scales of budgets and sedIment archives

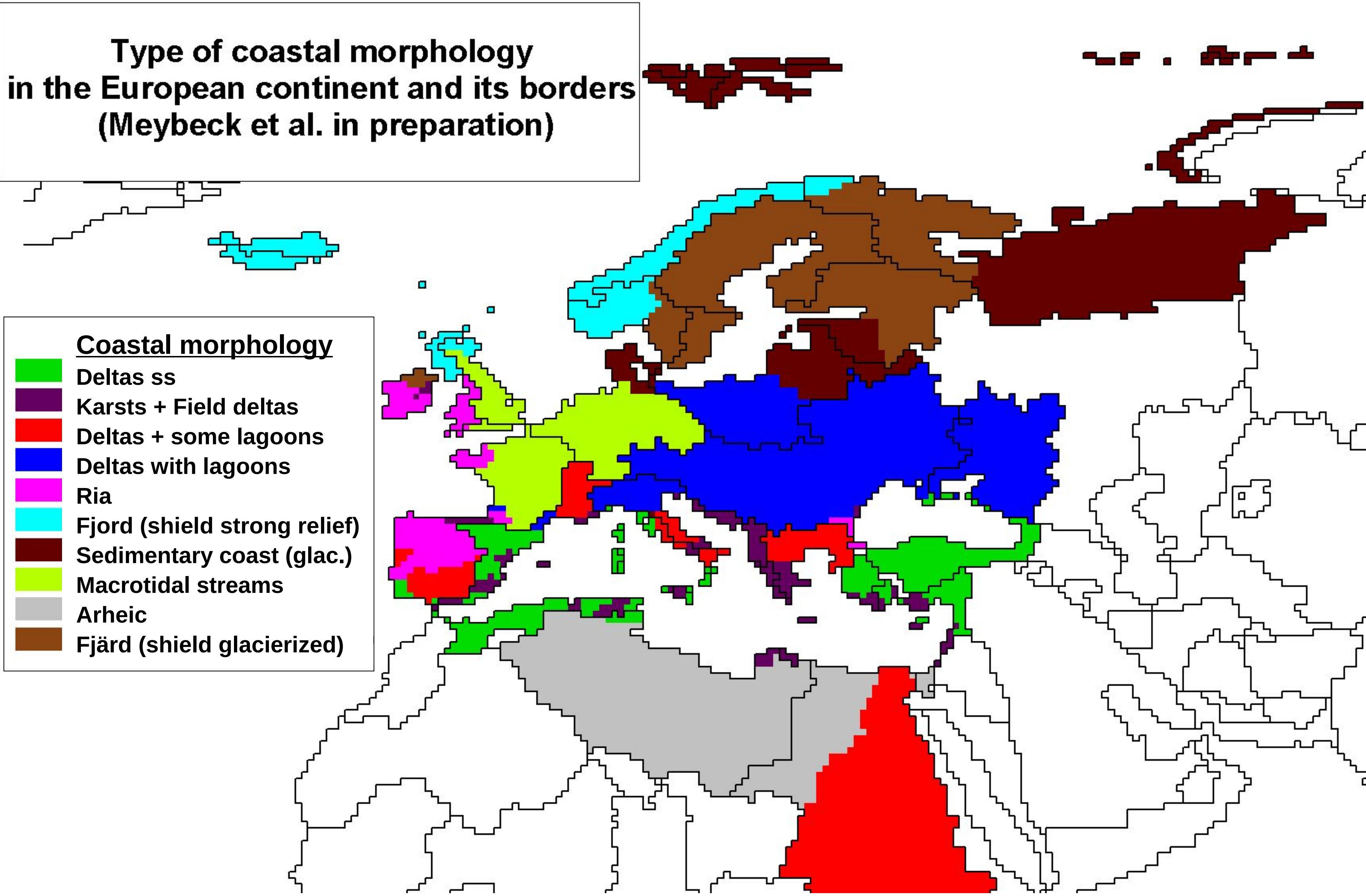


S1, S2, S3 → River stations

A1, A2, A3, A4, A5 → Sediment archives

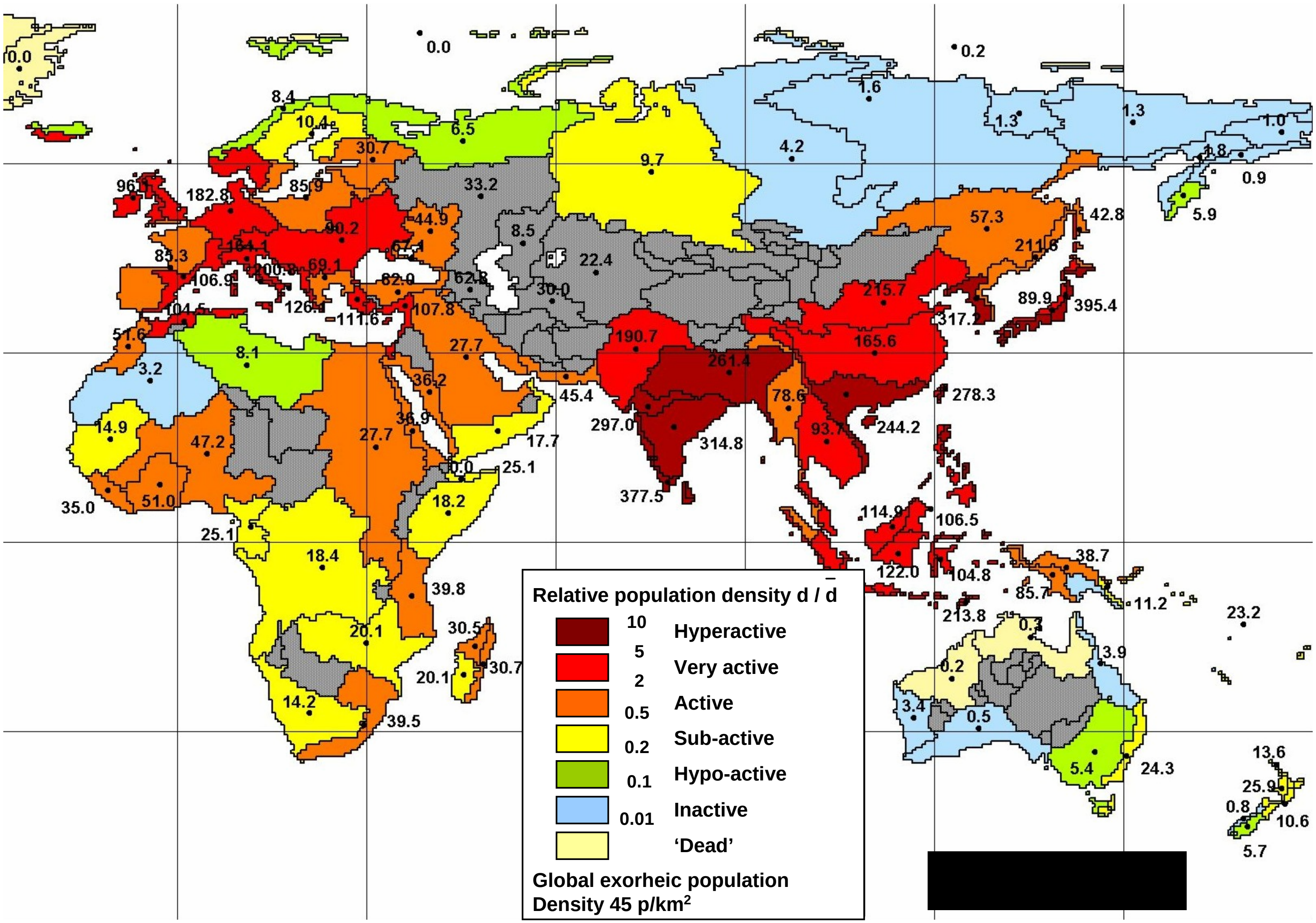
River stations and sediment archives capture different information on the natural sources and sinks of particulate matter

European Coast and riverine fluxes



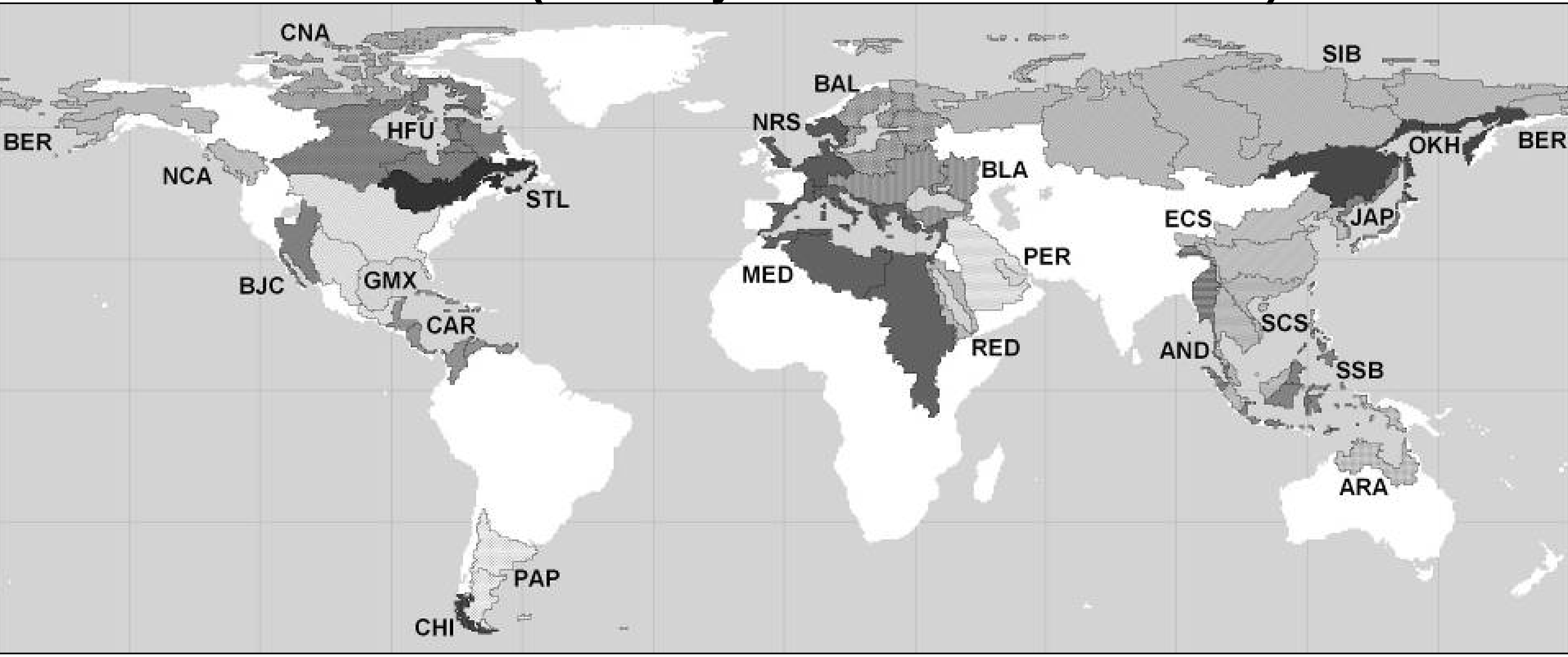
Coastal zone segmentation

Relative population density for coastal basins



[redacted]

FYI: River catchments and criteria of major regional seas (RS) and other mega filters of land to ocean fluxes (after Meybeck et al. 2007 MarChem)



- Quasi-enclosed RS (C1) : BAL = Baltic; BLA = Black-Azov; MED = Mediterranean; HFU = Hudson / Foxe / Ungawa; JAP=Japan; BJC= Gulf of California; PER=Persian Gulf; RED=Red Sea
- Semi-enclosed RS (C2) : SCS = SouthChina Sea; GMX = Gulf of Mexico; SSB = Sunda / Sulu / Banda
- Open RS (C3) : NRS = North Sea; STL = Saint Lawrence Gulf; CAR = Caribbean; BER = Bering; OKH = Okhotsk; AND = Andaman; ARA = Arafura; ESC = East China Sea (C1 – C3)
- Archipelago coasts (C4) : CAN = Canadian Archipelago; NCA = North Cascadia Basin; CHI = South Chile
- Extended platforms (C5) : SIB = Siberian Seas; PAP = Patagonia Platform.

Total retention of river material by RS – without estuarine filter

	Sediment input	Nitrogen preindustrial	Nitrogen contemporary	SiO_2 natural
	% of total flux to coastal zone retained			
Filters C_1 to C_3	32.6	26.8	33.9	25.1
Filters C_1 to C_5	33.7	28.4	35.7	26.4

→ compared to 8.7 % and 2.5 % of global ocean area and volume

→ amount of river material received per unit area / volume is actually 10 to 30 times higher than for open oceans

Meybeck, Dürr, Roussennac, Ludwig (Marine Chemistry, in revision)

CONCLUSION (1)

- GLOBAL RIVER METAL CONTENTS CAN NOW BE SPLIT BETWEEN PRISTINE AVERAGES AND CONTEMPORARY LEVELS
- PRISTINE LEVELS OF HEAVY METALS ARE VERY CLOSE TO SHALES AVERAGES.AT THE FINE SCALE THEYDEPEND ON LITHOLOGY
- CONTEMPORARY LEVELS DEPEND ON (1)PRESSURES(population density),(2)ENVIRONMENTAL PROTECTION,(3)SEDIMENT YIELDS
- FLUXES OF EXCESS METAL NOW ALSO DEPEND ON SEDIMENT RETENTION IN BASINS(damming)
- EUROPEAN BASINS WERE EXTREMELY CONTAMINATED IN THE 1960s DUE TO HIGH PRESSURES AND LOWDILUTION CAPACITIES
- Cd,Hg,then,Zn,Pb ARE MOST SENSITIVE TO HUMAN IMPACTS,Cu,Cr and Ni ARE LESS SENSITIVE

CONCLUSION (2)

- **DETAILED STUDIES OF METAL CIRCULATION IN BASINS SHOW THAT MATERIAL FLOWS EXCEED 10 TO 1000 TIMES THE EXCESS METAL LOADS CARRIED BY RIVERS(leakage ratio)**

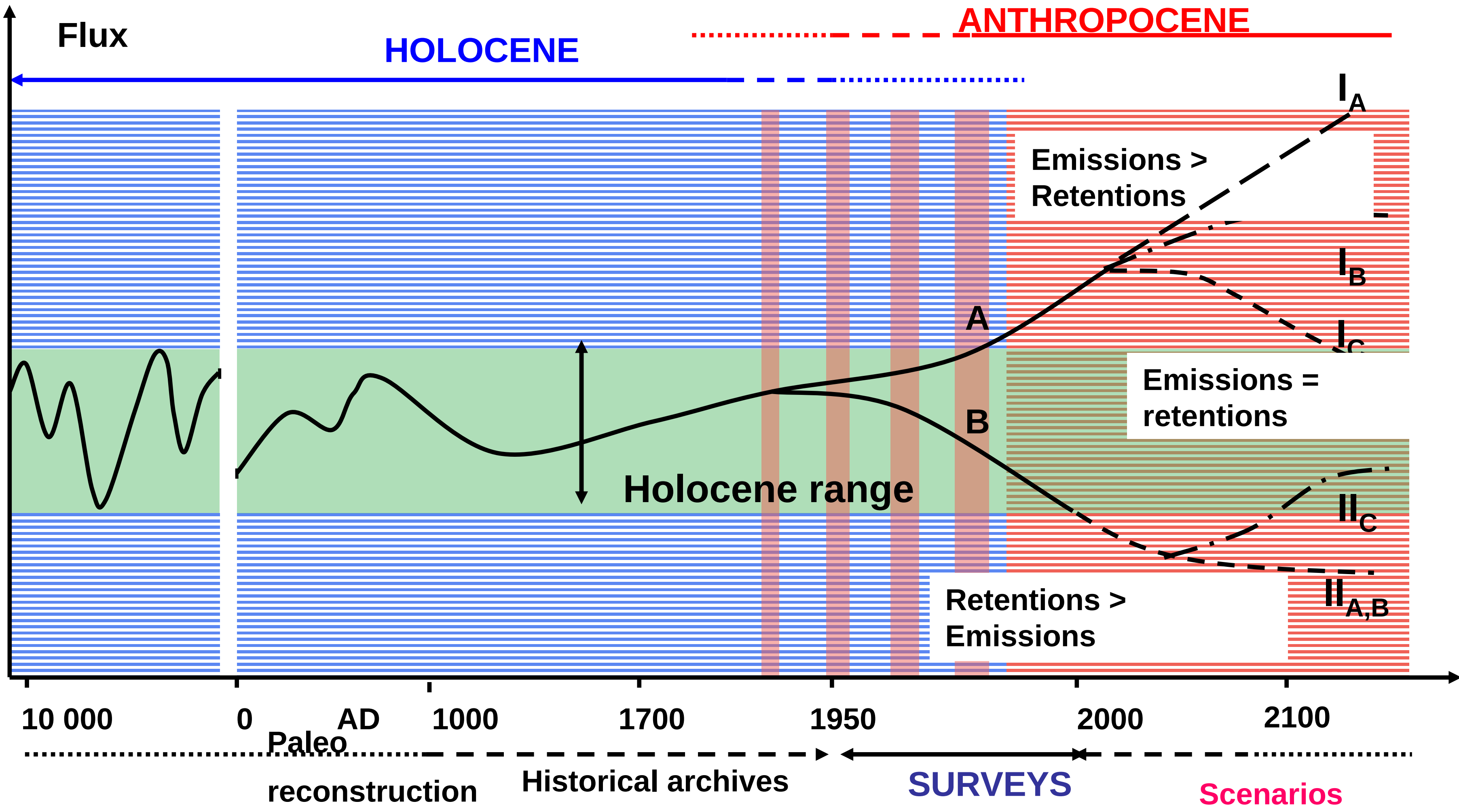
- **IN A GIVEN BASIN EACH METAL HAS ITS OWN CONTAMINATION TRAJECTORY DEFINED BY PRESSURES/DILUTION FACTORS**

- **IN WESTERN EUROPE AND IN USA THE DECONTAMINATION IS VERY EFFECTIVE SINCE THE1970s**

- **FUTURE TRENDS OF METAL INPUTS TO OCEAN SHOULD NOW BE BASED ON REGIONAL ANALYSES,TAKING INTO ACCOUNT PRESSURES SCENARIOS**

- **DUE TO THE GROWING COASTAL LOCATION OF MEGACITIES DIRECT INPUTS OF METALS TO ESTUARIES,i.e. not through river basins,ARE LIKELY TO INCREASE**

Trajectories of riverine fluxes of metals during the Holocene and Anthropocene (accelerated time scale)



Multiple trajectories are possible,depending on emissions / retention ratio