



HAL
open science

Historical records, sources, and spatial trends of PCBs along the Rhône River (France)

Brice Mourier, Marc Desmet, Peter C. van Metre, Barbara J. Mahler, Yves Perrodin, Gwenaëlle Roux, Jean-Philippe Bedell, Irene Lefevre, Marc Babut

► **To cite this version:**

Brice Mourier, Marc Desmet, Peter C. van Metre, Barbara J. Mahler, Yves Perrodin, et al.. Historical records, sources, and spatial trends of PCBs along the Rhône River (France). *Science of the Total Environment*, 2014, 476-477, pp.568-576. 10.1016/j.scitotenv.2014.01.026 . halsde-00944281

HAL Id: halsde-00944281

<https://hal.science/halsde-00944281>

Submitted on 16 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Historical records, sources, and spatial trends of PCBs along the Rhône River (France)

Brice Mourier ^a, Marc Desmet ^b, Peter C. Van Metre ^c, Barbara J. Mahler ^c, Yves Perrodin ^a,
Gwenaëlle Roux ^a, Jean-Philippe Bedell ^a, Irène Lefèvre ^d, and Marc Babut ^e

^a Université Lyon 1, UMR 5023 Ecologie des Hydrosystèmes Naturels et Anthropisés, ENTPE,
CNRS, 3, Rue Maurice Audin, 69518 Vaulx-en-Velin, France

^b Université de Tours, GÉHCO EA 6293, 37000 Tours, France

^c U.S. Geological Survey - 1505 Ferguson Lane, Austin, TX, USA 78754

^d UMR 8212(CEA, CNRS, UVSQ), LSCE, Bât. 12, avenue de la Terrasse, F-91198 Gif-sur-Yvette
Cedex, France

^e Irstea - UR MALY, rue de la Doua, CS70077, F-69626 Villeurbanne, France

brice.mourier@unilim.fr

marc.desmet@univ-tours.fr

pcvanmet@usgs.gov

bjmahler@usgs.gov

yves.perrodin@entpe.fr

gwenaelle.roux@entpe.fr

jeanphilippe.bedell@entpe.fr

irene.lefevre@lsce.ipsl.fr

marc.babut@irstea.fr

Corresponding author: Brice Mourier

Present adresse:

University of Limoges

Groupement de Recherche Eau Sol Environnement

123 Avenue ALBERT THOMAS

87060 LIMOGES CEDEX

e-mail address: brice.mourier@unilim.fr

Abstract

Despite bans on PCB use since 1975 (open systems) and 1987 (closed systems), concentrations of PCBs in riverine fish in France continue to exceed regulatory levels. We present historical records of PCB concentrations in sediment cores from eight sites on the Rhône River, from Lake Geneva to the Mediterranean Sea. Maximum PCB concentrations (sum of seven indicator PCBs) increase downstream, from 11.50 µg/kg at the most upstream site to 417.1 µg/kg at the most downstream site. At some sites peak concentrations occur in sediment deposited as recently as the 2000s. Hierarchical clustering (five clusters) identified differences in PCB congener profiles within and between sites. Exponential models fit to decadal time windows indicate that rapid reductions in concentrations during about 1990–2000 have slowed, and that it might be decades before target concentrations in sediment that correspond to regulatory thresholds in fish will be reached at some sites.

1. Introduction

Rivers receive a multitude of persistent organic pollutants (POP), including polychlorinated biphenyls (PCBs), that are transported principally by particulate matter (Viers et al., 2009). PCBs are released into the environment by improper disposal, leakage, incineration, and volatilization (Breivik et al., 2002). PCBs do not readily degrade, and can move through food webs and bioaccumulate in the fatty tissues of fish and mammals (Hammond et al., 1972). The chemical quality of sediment is a major concern for public policy makers and for stakeholders

1
2
3
4 (e.g., environmental managers, navigation and power supply companies) because of the
5
6
7 potential effects on aquatic biota and, ultimately, human health.

8
9
10 In France, PCBs still are of major concern (Agence nationale de sécurité sanitaire, 2011),
11
12 despite a ban in 1975 on their use in open systems (e.g., hydraulic fluids, coatings) and another
13
14 in 1987 on their use in closed systems (e.g., transformers, capacitors) (Chevreuil et al., 1988).
15
16 Contamination of sediment and fish by PCBs in the Rhône River system was reported as early as
17
18 the 1980s (Andre and Lascombe, 1988; Brodhag, 1989; Santiago et al., 1994). New regulation
19
20 on dioxins and related chemicals in foodstuffs was introduced in 2006 and amended in 2011
21
22 (European Commission, 2011), and it was reported that the load of dioxin-like PCBs in fish is
23
24 correlated to that of the sum of the so-called indicator PCB [International Union of Pure and
25
26 Applied Chemistry (IUPAC) congeners 28, 52, 101, 118, 138, 153, and 180] (ΣPCB_i)
27
28 concentrations in sediment (Babut et al., 2009). This led to an extended investigation of fish
29
30 contamination throughout the Rhône River catchment (Babut et al., 2011; Babut et al., 2012)
31
32 and in other French river basins. As a result of PCB contamination, commercial fishing and fish
33
34 consumption currently (2013) are banned in the main channels of the Rhône and Saône (the
35
36 largest tributary to the Rhône River) Rivers from upstream of Lyon to the Mediterranean Sea,
37
38 and there are bans along reaches of numerous tributaries (Eaufrance, 2011).

39
40
41 Identification of long-term trends in PCB contamination can contribute to a better
42
43 understanding of current (2013) risks and can assist in evaluation of the effectiveness of
44
45 environmental legislation aimed at reducing the impact of human activities in the basin.

46
47
48 However, datasets at a multi-decadal time scale (e.g., 20–50 years) on PCBs in water, sediment,
49
50 and fish are not available for the Rhône River or, indeed, for most major rivers. One way to
51
52
53
54
55

1
2
3
4 overcome this limitation is to reconstruct contamination histories through the use of natural
5
6 sediment archives. In lakes and reservoirs with negligible post-depositional processes (e.g.,
7
8 bioturbation, porewater transport, biotransformation), sediments provide a record of
9
10 contaminant inputs and other environmental changes over decadal time scales (Eisenreich et
11
12 al., 1989; Van Metre et al., 1997; Van Metre and Mahler, 2005). In some riverine systems,
13
14 sediment accumulates in off-channel depositional zones over long periods, creating multi-
15
16
17
18
19
20
21 decadal records of contaminant histories (Van Metre et al., 1998; Desmet et al., 2012).

22 We have previously reported trends in PCBs in sediment cores from three secondary-
23
24 channel depositional areas along the Rhône River and one reference site (Desmet et al., 2012).
25
26 Here we expand that analysis to eight locations in the Rhône River basin to characterize the
27
28 contamination levels, sources (through the distribution of PCB congeners), and spatial and
29
30
31
32
33
34
35
36
37 temporal trends in PCBs at the basin scale.

38 **2. Methods**

39 **2.1 Site Selection**

40
41
42
43
44 Sites for collection of sediment cores were chosen to evaluate the upstream-downstream
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

52 Sediment cores were collected during May 2008–February 2011 at eight sites in or adjacent to
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

1
2
3
4 sites currently (2013) are connected to the Rhone River and likely subject to continual sediment
5
6
7 deposition.

8
9
10 The two most upstream sites, Gravière des Etournels (site ETL) and MTE, are in a
11
12 relatively non-industrialized part of the Rhône River basin (fig. 1). Site ETL is 23 km downstream
13
14 from Lake Geneva, and is a former quarry that became inundated when it was abandoned in
15
16 1980 (Supplementary Information fig. S1). Site MTE is 104 km downstream from Lake Geneva
17
18 and is in a secondary channel at the downstream end of a cutoff meander of the Rhône River
19
20 that is open to the river at its downstream end (Supplementary Information fig. S2). The Grand
21
22 Large (site GDL, Supplementary Information fig. S3) and site CPX (Supplementary Information
23
24 fig. S4) sites (171 and 175 km downstream from Lake Geneva, respectively) are downstream
25
26 from site MTE and upstream from Lyon. GDL is a small reservoir of 160 Ha (the main part of the
27
28 river is diverted around Grand Large), and site CPX is an inundated former quarry adjacent to
29
30 the old channel of the Rhône River upstream from Lyon. Both sites are assumed to record the
31
32 effects of PCB inputs from a PCB treatment (incineration facility about 40 km upstream from
33
34 Lyon, smaller cities between Lyon and site MTE, the Bourbre River, and non-point emissions
35
36 from the northern part of the greater Lyon urban area. These four sites (ETL, MTE, GDL, and
37
38 CPX) are referred to hereinafter as upstream sites.
39
40
41
42
43
44
45
46
47

48
49 Four sites are downstream from Lyon. Table Ronde (TBR), 12 km downstream from the
50
51 confluence of the Rhône and Saône Rivers in Lyon, is a small embayment on the right bank that
52
53 is open to the old Rhône River channel at its downstream end (Supplementary Information fig.
54
55 S5). Ile du Beurre (site BRE) is 22 km downstream from TBR, and is in a secondary channel in a
56
57 forested wetland adjacent to the Rhône River (Supplementary Information fig. S6). Site BRE was
58
59
60
61
62
63
64
65

1
2
3
4 chosen because of its location downstream from the Lyon metropolitan area and the industrial
5
6
7 corridor that extends to the south of the city. It also is downstream from the confluence with
8
9
10 the Gier River (fig. 1), which, like the Bourbre River, has a comprehensive ban in place on the
11
12
13 consumption of fish because of PCB contamination (Eaufrance, 2011). Arras (ARS) is 41 km
14
15
16 downstream from site BRE and upstream from the city of Valence, is an off-channel basin
17
18
19 created by the construction of a dam in 1971, and is open to the old Rhône River channel at its
20
21
22 downstream end (Supplementary Information fig. S7). The most downstream site, Lône de la
23
24
25 Grange Ecrasée (site GEC), is a secondary channel downstream from the confluence with the
26
27
28 Isère River (Supplementary Information fig. S8). The watershed of the Isère River includes
29
30
31 several historical PCB production and disposal facilities. These four sites (TBR, BRE, ARS, and
32
33
34 GEC) are referred to hereinafter as downstream sites.

35 **2.2 Core collection and sediment description**

36
37
38 Before coring, the study sites were surveyed using a GPSMAP® 521s sounder (Garmin Ltd.,
39
40
41 Southampton, UK) to map the depth of the water. Several short cores were taken and
42
43
44 inspected visually to evaluate the spatial nature and extent of major sedimentary facies. Water
45
46
47 depth and the reconnaissance cores were used to guide site selection and coring locations.
48
49
50 Sediment cores were collected with a UWITEC® corer (Uwitec, Mondsee, Austria) fitted with a
51
52
53 2.0-m-long, 63-mm- or 90-mm-diameter plastic liner with a core catcher at the bottom. From a
54
55
56 cataraft, an extension rod was used to push the corer gently into the sediments. Multiple 63-
57
58
59 mm diameter cores were collected at sites MTE, CPX, and BRE. 90-mm-diameter cores were
60
61
62
63
64
65

1
2
3
4 collected at each of sites ETL, GDL, TBR, BRC, ARS, and GEC, and all descriptions and
5
6
7 measurements for each site were performed on the same core.
8

9
10 Sediment cores ranged in length from 0.5 to 1.40 m. Core liners were cut near the
11
12 sediment-water interface and capped for transport to the laboratory. At the laboratory, cores
13
14 were sub-sampled at a 1-cm interval for grain size analysis and at a 3- or 4-cm interval for
15
16 analysis of PCBs, total organic carbon (TOC), and radionuclides. For each of sites ETL, MTE, GDL,
17
18 TBR, ARS, and GEC cores, all sub-samples for analysis of PCBs, TOC, radionuclides, and grain-size
19
20 distribution were obtained from one core. At sites CPX and BRE, sub-samples from one core
21
22 were analyzed for PCBs, TOC, and grain-size distribution (primary core) and samples from a
23
24 second core were analyzed for grain-size distribution and radionuclides (radionuclide core).
25
26 Grain-size distribution was used at sites CPX and BRE to help correlate the primary and
27
28 radionuclide cores so that dates could be assigned to the primary core.
29
30
31
32
33
34

35 Dry bulk density was determined as the difference between wet and dry mass divided by
36
37 the volume of the container. Grain-size distributions were determined by sonicating and then
38
39 analyzing each sample with a Mastersizer 2000[®] laser mounted with a hydro SM small-volume
40
41 dispersion unit (Malvern Instruments, Worcestershire, UK) . Grain-size mean, mode, sorting,
42
43 and skewness were computed using the Gradistat program (Blott and Pye, 2001). Cumulative
44
45 volumetric percentages of sand (>63 μm), silt (4–63 μm), and clay (<4 μm) were determined for
46
47 each depth interval (< 63 μm , i.e. silt and clay together, hereinafter fine fraction).
48
49
50
51
52
53

54 **2.3 Analytical methods**

55
56
57 Sediment samples were analyzed for radionuclides at the Laboratoire des sciences du climat et
58
59 de l'environnement (LSCE), Gif sur Yvette, France. Following drying, sub-samples from each
60
61

1
2
3
4 core were analyzed for radionuclides by counting for at least 24 hours using low-noise gamma
5
6 spectrometry. Gamma emissions were detected with a germanium detector and used to
7
8 quantify specific activities of ^{226}Ra , ^{228}Ra , ^{40}K , ^{210}Pb , and ^{137}Cs (Pinglot and Pourchet, 1995).
9
10

11
12 Samples were prepared for measurement of organic carbon by drying, sieving to 2 mm,
13
14 and grinding to $<200\ \mu\text{m}$, in accordance with standard NF ISO 11464 (Groupement d'Etudes
15
16 Méthodologiques pour l'Analyse des Sols, 2011), and acidifying with aqua regia (a mixture of
17
18 concentrated nitric and hydrochloric acids). Total organic carbon was analyzed by high-
19
20 temperature combustion ($1,250^\circ\text{C}$) in accordance with standard NF ISO 10694 (Groupement
21
22 d'Etudes Méthodologiques pour l'Analyse des Sols, 2011).
23
24
25
26

27
28 PCBs were analyzed by the EUROFINs laboratory, Saverne, France (www.eurofins.fr),
29
30 which is accredited in accordance with ISO 17025. In brief, 5 g of dried, homogenized sediment
31
32 was extracted for a minimum of 8 hours with toluene/acetone (90/10 v/v) in a Soxhlet
33
34 apparatus. A mixture of isotope-labelled internal standards used for identification and
35
36 quantification of native congeners was added prior to extraction. The sample extract
37
38 underwent a clean-up step using gel permeation chromatography. Clean-up consisted of
39
40 sequential passes through silica, aluminium oxide, Florisil, and active carbon columns. Prior to
41
42 extraction, the standard 13C12-123789-HexaCDD was injected to allow the quantification of
43
44 isotopic labels. The sample extract was analyzed by high resolution gas chromatography-high
45
46 resolution mass spectrometry (HRGC/HRMS) with a VG-AutoSpec in selected ion monitoring
47
48 (SIM) mode. Laboratory quality control consisted of periodic analysis of blanks and certified
49
50 reference materials. Analytical results for environmental samples were not blank-corrected.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 The interpretations that follow are based on ΣPCB_i , commonly used in European national
5
6 regulations to ensure food safety (e.g., Royal Order, 2000). Quantification limits for PCB_i ranged
7
8 from 0.02 $\mu\text{g}/\text{kg}$ (PCB 52) to 0.05 $\mu\text{g}/\text{kg}$ (PCB 153).
9
10

11 12 13 14 15 **2.4 Statistical methods** 16 17

18
19 Hierarchical clustering (Ward's method) was used to classify the samples according to
20
21 their congener compositions (Ward, 1963); this method of hierarchical clustering gives compact
22
23 clusters and clear hierarchies (Aitchison, 1986; Martin-Fernandez et al., 1998). Relative
24
25 concentrations of PCB congeners (% of ΣPCB_i) were used so that the magnitude of the
26
27 concentrations would not influence the result. Distances between PCB congener compositions
28
29 were measured as Euclidean distances between centered log ratios (CLR) (Aitchison et al.,
30
31 2000). The results were interpreted from a dendrogram, a branching diagram that represents
32
33 the relationships of dissimilarity among a group of entities. Following clustering, compositional
34
35 differences between clusters were evaluated using a discriminant analysis (DA) (Kachigan,
36
37 1991). Discriminant analysis is a statistical procedure for identifying boundaries between
38
39 groups (here, clusters) of objects (here, samples) on the basis of quantitative predictor
40
41 variables (here, PCB congeners). The objects are expressed as linear combinations (factors) of
42
43 the predictor variables; the centroid of each group in the factor space is determined and the
44
45 probability that each object is classified into the correct group is evaluated. The confusion
46
47 matrix evaluates the consistency of classification of samples into groups by the clustering and
48
49 DA methods, providing a measure of confidence in the results. Data preparation and
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 multivariate analysis were performed by using CoDaPack V2 (Thió-Henestrosa and Martín-
5
6
7 Fernández, 2005) and XLSTAT V3.05 (Addinsoft, Paris, France), respectively.
8

9
10 To evaluate spatial trends in PCB contamination at the Rhône River basin scale, PCB_i
11
12 concentrations for three time windows were evaluated relative to distance downriver, i.e., from
13
14 the outlet of Lake Geneva. Regression models (exponential, linear, and piecewise linear) were
15
16
17 fit to median values for the three time windows for which there are data from a sufficient
18
19
20 number of sites (1986–1995, 1996–2005, and post 2005).
21
22
23
24

25 **3. Results**

26 **3.1 Age Dating**

27
28 Peak ¹³⁷Cs activity, a primary date marker, was used to estimate sediment deposition dates in
29
30 the cores. Two date-depth markers inferred from the ¹³⁷Cs profile can be identified in European
31
32 sediment cores: a peak in ¹³⁷Cs activity (1963) corresponding to the height of releases
33
34 associated with world-wide nuclear weapons testing (Beck and Helfer, 1990), and a second
35
36
37 (1986) peak corresponding to the Chernobyl accident. The Chernobyl ¹³⁷Cs peak was identified
38
39 in almost all of the cores (Supplementary Information figs. S1–9). Changes in grain-size
40
41
42 distribution provided secondary date markers. Changes were interpreted as indicating onset or
43
44
45 cessation of a land-use activity (e.g., quarrying), timing of major flood events, or a change in
46
47
48 connection with the Rhône River (sites ETL, CPX, and BRE) (Supplementary Information fig. S1,
49
50
51 S3, S6–9). Flood-event facies identified in the cores were matched to flood flows measured at
52
53
54 the nearest streamflow-gauging station (Ternay or Viviers, fig. 1).
55
56

57 Age dates for MTE, CPX, and BRE cores, presented in Desmet et al. (2012), were based
58
59 on ¹³⁷Cs peaks and changes in grain size matched to floods. Age dates for the ETL core were
60
61

1
2
3
4 based on a ^{137}Cs maximum at a depth of 44–45 cm interpreted as the Chernobyl accident and
5
6
7 an increase in the percentage of silt and clay at a depth of 72–73 cm in the core, interpreted as
8
9
10 indicating the cessation of quarrying (Supplementary Information fig. S1). Age dates for the GDL
11
12 core were estimated on the basis of the ^{137}Cs profile and on variations in grain size
13
14
15 corresponding to dredging in 2005 (Supplementary Information fig. S3). However, the age-
16
17 depth model was difficult to define at this site because sediment deposition was disturbed by
18
19
20 reservoir management (Babut et al., 2011). At sites TBR and GEC, sediment deposition rates
21
22
23 were too high (or core lengths were too short) to observe the complete ^{137}Cs maximum related
24
25
26 to the Chernobyl accident. Estimated date of sediment deposition at these sites is based on
27
28
29 grain-size changes that correspond to floods that occurred in the early 1990s and 2000s
30
31
32 (Supplementary Information figs. S5, S8). Age dates for the ARS core were based on a single
33
34
35 pronounced ^{137}Cs peak that occurred at a depth of 95–97cm and interpreted as corresponding
36
37
38 to the Chernobyl accident (Supplementary Information fig. S7). The age model was refined on
39
40
41 the basis of a slight decrease in percentage of silt and clay in the upper part of the core that
42
43
44 matched well with floods in the early 2000s.

3.2 Indicator PCB (PCB_i) concentrations

45
46
47 PCB_i were measured in 248 sediment samples. Three or more congeners with
48
49
50 concentrations below the detection limit were measured in four samples; those samples
51
52
53 therefore were excluded from the dataset for statistical analysis. For two samples, the
54
55
56 concentration of an undetected congener (PCB 101) was estimated by multiplying the median
57
58
59 proportion of the congener in the adjacent layers by the sum of seven congeners in the layer
60
61
62
63
64
65

1
2
3
4 with the non-detection. Sediment samples deeper than 51 cm at site ETL (11 samples) were
5
6
7 excluded from statistical analysis because the deposits were interpreted as having been
8
9
10 remobilized (Supplementary Information fig. S1). Samples with an absolute standardized
11
12 residual greater than 2 (“outliers”) were evaluated: two were excluded (one collected from
13
14 site BRE and the other from site ARS) from subsequent statistical analysis because the total PCB
15
16 concentration was atypically high relative to that in adjacent layers, and because the PCB
17
18 profile (in both cases, a presumed positive bias of PCB 52) was not consistent with that of most
19
20 of the other measurements.
21
22
23
24

25 PCB_i concentrations and profiles varied considerably within and between the sites
26
27 sampled for this study, both in timing and magnitude of peak concentrations (fig. 2 and 3).
28
29
30 Maximum PCB_i concentrations were lowest upstream (e.g., maximum Σ PCB_i concentration of
31
32 11.50 $\mu\text{g}/\text{kg}$ at ETL) and increased downstream to a concentration of 417.1 $\mu\text{g}/\text{kg}$ at GEC (fig. 3).
33
34
35 Maximum concentrations measured for this study exceeded those measured in sediment in
36
37 several other European rivers, such as the Sava River (the largest tributary to the Danube) (<4
38
39 $\mu\text{g}/\text{kg}$) (Heath et al., 2010), the Vistula River, Poland (64 $\mu\text{g}/\text{kg}$) (Dmitruk et al., 2008), and the
40
41 Po River, Italy (4.1 $\mu\text{g}/\text{kg}$) (Viganò et al., 2008).
42
43
44

45 Temporal patterns of Σ PCB_i concentrations vary from upstream to downstream.
46
47
48 Concentrations at site MTE are highest in the 1970s and decrease monotonically to the top of
49
50 the core; concentrations at site ARS generally decrease from the mid-1980s on. Concentrations
51
52 in PCB concentrations at the other six sites are more variable. At ETL, CPX, BRE, and GEC,
53
54 concentrations of PCBs were elevated and variable in the late 1980s and mid-1990s, decreased
55
56 in the late 1990s, and have remained relatively stable since. At GDL and TBR, maximum
57
58
59
60
61

1
2
3
4 concentrations occurred in the 2000s (ΣPCB_i of 159.8 $\mu\text{g}/\text{kg}$ in 2003 at GDL and 131.5 $\mu\text{g}/\text{kg}$ at
5
6 TBR in 2007). At GDL, a progressive increase occurred in the early 1980s until 2005, but the
7
8
9 ΣPCB_i maximum at TBR was brief, occurring only during 2007–08.

14 **3.3 Spatial trends in PCBs at the scale of the Rhône River and changes through time**

17 Exponential regression models used to evaluate changes in PCB concentrations in a
18
19 downstream direction for three time windows (1986–1995, 1996–2005, and post 2005)
20
21 provided a good fit to the data ($r^2 = 0.92$, $r^2 = 0.96$, $r^2 = 0.94$, respectively; $p = 0.03$). Site GDL was
22
23 excluded from this regression because its age model was not consistent with those from the
24
25 other sites (Supplementary Data fig. S3). Linear and piecewise linear regression models had
26
27 acceptable but lower r^2 (0.71–0.96), and residuals were substantially higher than those from the
28
29 exponential models.
30
31
32
33

34
35 The exponential models illustrate spatial and temporal trends in PCB concentrations in
36
37 Rhône River sediment (fig. 4). PCB concentrations generally increase from upstream to
38
39 downstream, regardless of the period considered. Concentrations decreased substantially from
40
41 about 1986–95 to 1996–2005 and to a much lesser extent from 1996–2005 to post 2005—top of
42
43 core. The decreases are more marked at downstream sites than at upstream sites. The
44
45 apparent slowing of the rate at which PCBs are decreasing indicates that PCB inputs to the
46
47 Rhône River might be continuing, particularly downstream from the greater Lyon area.
48
49
50
51
52

53 Median ΣPCB_i values for downstream sites TBR and BRE for the 1986–95 time window
54
55 diverge from the exponential model for this period (fig. 4). The median for TBR is less than that
56
57 predicted by the regression model for this period, whereas the median for BRE is greater than
58
59
60
61

1
2
3
4 that predicted (and greater than that predicted by the exponential models, to a lesser extent,
5
6
7 for the 1996–2005 and post-2005 time windows). The watershed of the Rhône River
8
9
10 downstream from the city of Lyon is much larger than it is upstream, because it also includes
11
12 the watershed of the Saône River, whose confluence with the Rhone River is at the downstream
13
14 end of Lyon (fig. 1). A mean ΣPCB_i concentration of 18.7 $\mu\text{g}/\text{kg}$ ($n= 6, \pm 16.6$) was measured in
15
16
17 sediments samples collected from the downstream end of the Saône River after 2007
18
19
20 (Eaufrance, 2011). The change in watershed size might explain the considerable dilution of PCB
21
22 concentrations observed at TBR. Conversely, at BRE and downstream, local PCB sources might
23
24
25 be superimposed on the general contamination pattern.
26
27
28
29
30
31
32

33 **3.4 PCB congener profiles**

34
35 Cluster analysis provides some insights into patterns of PCB congeners. On the basis of the
36
37 dendrogram distances (Supplementary Information fig. S10), all samples were assigned to one
38
39 of five clusters. Cluster 4 and 5 contained the most samples ($n=97$ and 70 , respectively), and
40
41
42 clusters 1, 2 and 3 contained far fewer ($n=21$, 18 , and 25 , respectively). In the DA, two factors
43
44
45 were sufficient to describe 97% of the variance; the separation of the PCB congeners in the
46
47 two-dimensional factor space indicated that samples were distinguished to a large extent by
48
49
50 degree of biphenyl chlorination (Supplementary Information figs. S10 and S11a). The confusion
51
52
53 matrix confirmed the integrity of the clustering: less than 10% of the cluster analysis
54
55
56 classifications were reclassified into a different cluster by the DA (Supplementary Information
57
58
59 fig. S11b and 11c).
60
61
62
63
64
65

1
2
3
4 Despite variability within and between sites, some patterns among PCB profiles can be
5
6 identified (fig. 3). Cluster 1 is characterized by low-chlorinated biphenyls (PCB 28, 52, and 101),
7
8 and samples in cluster 1 mostly are from GEC, the most downstream site. In the GEC core, the
9
10 dominance of cluster 1 extends from about 1990 to the top of the core. Cluster 2 is composed
11
12 mainly of *tetra-penta*-chlorinated biphenyls (PCB-52, PCB-101, and PCB-118). This assemblage,
13
14 characterized by relatively low-chlorinated biphenyls, was common for GDL samples deposited
15
16 from the 1980s to 2005. Congener profiles at sites GEC and GDL differ from those at other sites,
17
18 indicating that PCB contamination at these sites might be affected by local sources. Samples in
19
20 cluster 3 are primarily samples from the lower parts of cores collected from sites CPX and BRE,
21
22 and, to a lesser extent, from cores collected from sites TBR and GEC. These sediment intervals
23
24 correspond to flood deposits in the early 1990s and 2000s at sites CPX, TBR, and GEC
25
26 (Supplementary Information figs. S3, S5, and S8) and to removal of debris in 1984 at site BRE
27
28 (Supplementary Information fig. S6). Cluster 4 is dominated by *penta-hexa-hepta*-chlorinated
29
30 biphenyls (PCB-118, PCB-138, PCB-153, and PCB-180), and more samples are in cluster 4 than in
31
32 any other cluster. Samples in cluster 4 are abundant at upstream sites ETL, MTE, and CPX, and
33
34 at downstream site TBR (sediment deposited prior to 2007). Cluster 5 is characterized by high
35
36 proportions of *hexa*- and *hepta*-chlorinated biphenyls (PCB-153 and PCB-180). Upstream site
37
38 samples in cluster 5 consist of deeper sediments collected at site MTE and the most recently
39
40 deposited sediment collected at site CPX. Downstream site samples in cluster 5 include recently
41
42 deposited sediments represented by TBR, BRE, and ARS cores. Recently deposited sediments in
43
44 the TBR core, which include the PCB maximum, are in cluster 5 whereas older sediments are in
45
46 cluster 4.

4. Discussion

4.1 Implication for sources

A general upstream-downstream pattern of increasing PCB concentrations indicates a relation between PCB contamination and drivers, such as the catchment area or the cumulative upstream population (fig. 4B). Cumulative area and upstream population are correlated ($r^2 = 0.985$, $p < 0.0001$), and we hypothesize that they are proxies for emissions, as suggested by others (e.g., Breivik et al., 2002). However, population is neither the only nor the main driver of trends in historical PCB concentrations along the upstream-downstream gradient. Regardless of the decade, considerable variations are observed between the median concentrations, the models, and the cumulative population.

Trends in PCBs at sites MTE and ARS are consistent with widely reported patterns in PCB contamination (e.g., Eisenreich et al., 1989; Van Metre et al., 1997) in which the highest concentrations coincide with maximum use and environmental release in the 1960s and 1970s and marked decreases since. At other Rhône River sites, however, relatively high concentrations persist into the 1990s, inconsistent with this pattern, indicating that PCB inputs might have continued to occur in the basin following regulation. The PCB peak at TBR during 2007-08 is an example of this (fig. 3). We hypothesize that local PCB releases (in addition to those from the PCB treatment facility upstream from Lyon) have occurred upstream from this site in the past decade.

PCB distribution and trends also are affected by sediment flushing events and floods. Floods can cause bank erosion, resulting in inputs of less-contaminated sediment in some cases,

1
2
3
4 or in inputs of more-contaminated sediment in others (e.g., Lecce and Pavlowsky, 1997; Rozan
5
6
7 and Hunter, 2001). Floods also can mobilize upstream PCB sources, and major hydro-
8
9
10 sedimentary events therefore can affect congener compositions. At sites CPX, TBR, and GEC,
11
12 the data indicate a mixed congener assemblage (cluster 3) that corresponds to flood deposits.
13

14
15 A potential PCB point source to sediments deposited at sites GDL, CPX, and downstream
16
17 is the PCB treatment facility upstream from Lyon (fig. 1), which is authorized to release small
18
19 amounts of PCBs into the Rhône River (Eaufrance, 2011). Because PCBs are treated and
20
21 disposed of at this facility, its regulation differs from that of PCB use in France. The magnitude
22
23 and timing of PCB discharges at the facility are consistent with temporal trends in PCBs at site
24
25 CPX (Desmet et al., 2012), but they are more difficult to interpret at site GDL. At site GDL, PCB
26
27 concentrations increased until 2005 and the congener mixture (cluster 2, higher proportions of
28
29 low-chlorinated biphenyls) is distinct from that at the other sites. The trend at site GDL might
30
31 be attributable to PCB inputs from upstream tributaries (e.g., the Bourbre River) and (or)
32
33 management operations in the Grand Large (e.g., dredging). Mean ΣPCB_i concentrations
34
35 measured in surficial sediment of the Bourbre River range between 201.3 $\mu\text{g}/\text{kg}$ (1986–1995)
36
37 and 25.9 $\mu\text{g}/\text{kg}$ (post-2005) (Eaufrance, 2011).
38
39
40
41
42
43
44

45
46 Overall, PCB_i concentrations are higher at sites downstream from Lyon (TBR, BRE, ARS,
47
48 and GEC) than at sites upstream from Lyon (ETL, MTE, GDL, and CPX). This pattern indicates
49
50 that, although the PCB treatment facility is a source, it is neither the only source nor the most
51
52 important. The substantial increase in PCB_i concentrations in the downstream direction can be
53
54 explained only by other PCB sources in the greater Lyon metropolitan area and from tributaries
55
56 to the Rhône River downstream from Lyon. Potential sources include the city of Lyon, the
57
58
59
60
61

1
2
3
4 industrial corridor downstream from Lyon, the Gier River (a tributary that flows into the Rhône
5
6 River between TBR and BRE), the Isère River (a tributary that flows into the Rhône River at
7
8 Valence, between ARS and GEC), and perhaps other tributary watersheds (fig. 1), consistent
9
10 with sources evoked by Santiago et al. (1994). High concentrations of PCBs were measured in a
11
12 sediment core collected from the Gier River (ΣPCB_i of 115–160 $\mu\text{g}/\text{kg}$ since 1986 and up to 940
13
14 $\mu\text{g}/\text{kg}$ in the 1970s) (Babut et al., 2011) and in sediment from the Isère River (EauFrance, 2011).
15
16
17 The hypothesis of other PCB inputs from the Isère River is consistent with a difference in
18
19 congener mixture at site GEC (relatively low chlorinated congeners, cluster 1) relative to those
20
21 upstream (fig. 3). In the Rhône River delta, PCB concentrations are lower than in sediments
22
23 collected at site GEC for the most recent period (post-2005)—the mean ΣPCB_i for suspended
24
25 sediments collected since 2008 near the mouth of the Rhône River is 24.1 $\mu\text{g}/\text{kg}$ (n=122)
26
27
28 (EauFrance, 2011; SORA Station).
29
30
31
32
33
34
35
36
37

38 **4.2 Time and system recovery**

39
40 Results from this study and that of Desmet et al. (2012) provide empirical evidence that
41
42 environmental regulation of point sources enacted since 1975 and 1986 reduced the PCB
43
44 burden recorded in sediments. They also provide an indication of the time required for PCB
45
46 levels to decrease, particularly at downstream sites. Regulation of point sources, however, has
47
48 not prevented exceedances of the fish-consumption regulatory threshold set in 2008 and
49
50 revised in 2011 to 6.5 pg toxic equivalency factor (TEQ)/g wet weight (ww) for all species but
51
52 eel, for which the threshold was set at 10 pg TEQ/g ww (data for fish available at
53
54
55
56
57

58 <http://www.rhone-mediterranee.eaufrance.fr/usages-et->
59
60
61
62
63
64
65

1
2
3
4 [pressions/pollution_PCB/basepcb/index.php](#)) (European Commission, 2011). The question thus
5
6
7 arises: How much more time is required until PCB concentrations in surface sediment are
8
9 consistent with regulations for fish consumption? The ΣPCB_i concentration in sediment that
10
11 corresponds to the fish regulatory limit depends on the approach used and the data involved.
12
13
14 Using biota-sediment accumulation factors (BSAFs) over a large spatial scale, the sediment
15
16 benchmark for ΣPCB_i was determined to be 27 $\mu\text{g}/\text{kg}$ (Babut et al., 2012). At ΣPCB_i of 10 $\mu\text{g}/\text{kg}$,
17
18 75% of fish from 3 cyprinid species from 3 sites in the Rhône River along a contamination
19
20 gradient would match the regulatory threshold when applying the statistical model developed
21
22 by Lopes et al. (2011). We therefore consider ΣPCB_i of 10 and 27 $\mu\text{g}/\text{kg}$ as potential targets (fig.
23
24
25 4a).
26
27
28
29

30
31 At some sites the ΣPCB_i concentration in the most recently deposited sediments are less
32
33 than the lower target of 10 $\mu\text{g}/\text{kg}$, at others the ΣPCB_i concentration is between the two
34
35 targets, and at some sites ΣPCB_i concentration exceeds the upper target of 27 $\mu\text{g}/\text{kg}$
36
37 (Supplementary Information table S1). At sites ETL and MTE, ΣPCB_i concentrations at the
38
39 sediment surface (top of the core) already are below the lower target value and are still
40
41 decreasing (Desmet et al., 2012). At site CPX the concentration in the most recently deposited
42
43 sediment is just below the 10 $\mu\text{g}/\text{kg}$ target, and at site TBR it is between the two targets.
44
45
46 However, concentrations at site TBR are relatively constant before and after a brief peak in
47
48 concentration around 2008 (Supplementary Information fig. S5). Similarly, at site BRE there is
49
50 no trend in concentrations in recently deposited sediment (Desmet et al., 2012): Although
51
52 ΣPCB_i was less than the 27 $\mu\text{g}/\text{kg}$ target in 2003–04, ΣPCB_i increased to 55.12 $\mu\text{g}/\text{kg}$ in 2008.
53
54
55 This increase is related either to the same event as the maximum at TBR (consistent with the
56
57
58
59
60
61
62
63
64
65

1
2
3
4 similarity in PCB profiles, as indicated by the clustering) or to the modification of the sediment
5
6 deposition pattern at BRE (Supplementary Information fig. S6). At site ARS, the concentration at
7
8 the top of the core is near the 27 $\mu\text{g}/\text{kg}$ target, and concentrations have been decreasing since
9
10 1996 (Supplementary Information Table S1). The same pattern occurs at site GEC, with the
11
12 exception of a high outlier in 1999. Following the approach described in Van Metre et al.
13
14 (1998), we fit an exponential decay model to data from sites ARS and GEC from 1996 or 1998 to
15
16 2012 (Supplementary Information figs. S12 and S13). On the basis of these models, the
17
18 concentrations at the sediment surface might reach 27 $\mu\text{g}/\text{kg}$ ΣPCB_i in ~2014–2015 at ARS and
19
20 ~2020 at GEC. The more ambitious target of 10 $\mu\text{g}/\text{kg}$ might not be achieved before ~2045 at
21
22 ARS and ~2030 at GEC. The apparent lack of logic in this second prediction (given that GEC is
23
24 downstream of ARS) reflects the lack of data at concentrations between the two targets, which
25
26 hinders a prediction at this sensitivity, and the considerable scatter in the data. The scatter
27
28 likely arises from the fact that PCB concentrations at these sites are controlled by hydro-
29
30 sedimentary processes (mechanisms of deposition) and by several areas where PCBs might be
31
32 stored in the deposited sediments, i.e., the Rhône River and its tributaries.
33
34
35
36
37
38
39
40
41
42
43
44

45 **5. Conclusion**

46
47 Sediment cores from the Rhône River, from Lake Geneva to near the Mediterranean
48
49 Sea, provide a historical record of PCB inputs. The ^{137}Cs peak associated with the Chernobyl
50
51 accident identified in almost all of the cores provides a robust date marker. Large variability in
52
53 PCB trends and congener mixtures within these cores indicates that a complex combination of
54
55 sources and transport and (or) deposition patterns affect the PCB distribution. There are,
56
57
58
59
60
61
62
63
64
65

1
2
3
4 however, some broad patterns in these data. Much higher PCB_i concentrations downstream
5
6
7 from Lyon than upstream indicate that greater Lyon and some tributaries to the lower Rhône
8
9
10 River currently (2013) are the principle sources of PCBs to the river. Rapid decreases in PCB
11
12 concentrations that occurred between the mid-1980s and about 2000 have slowed, and it likely
13
14 will take a decade or more before PCB concentrations in sediment are consistent with
15
16
17 regulatory limits for fish consumption.
18
19
20
21

22 **Acknowledgements**

23
24 We thank Guillaume Fantino for providing spatial data and for many fruitful discussions. We
25
26
27 thank the five anonymous reviewers whose suggestions greatly improved the quality of the
28
29
30 manuscript. This project was funded by the Rhône-Mediterranean and Corsica Water Agency,
31
32
33 the Rhône-Alpes Region, the Provence-Alpes-Côte d'Azur Region, and the Compagnie Nationale
34
35
36 du Rhône (CNR) in the context of the Observatory of Rhône Sediments (OSR). These agencies
37
38
39 had no role in the study design; in the collection, analysis, or interpretation of data; in the
40
41
42 writing of the report; nor in the decision to submit the article for publication. Any use of trade,
43
44
45 firm, or product names is for descriptive purposes only and does not imply endorsement by the
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

References

- Agence nationale de sécurité sanitaire, 2011. <http://www.anses.fr/index.htm>, accessed July 12, 2011.
- Aitchison, J., 1986. The Statistical Analysis of Compositional Data. Mono-graphs on Statistics and Applied Probability. Chapman & Hall Ltd., London (UK). (Reprinted in 2003 with additional material by The Blackburn Press). 416 p. ISBN 1-930665-78-4.
- Aitchison, J., Barceló-Vidal, C., Martín-Fernández, J.A., Pawlowsky-Glahn, V., 2000. Logratio analysis and compositional distance. *Mathematical Geology* 32, 271-275.
- Andre, B., Lascombe, C., 1988. Qualité du fleuve Rhone, Synthèse des connaissances. Agence de l'Eau Rhone-Mediterranee-Corse, Lyon, France, 251 p.
- Babut, M., Miege, C., Villeneuve, B., Abarnou, A., Duchemin, J., Marchand, P., et al., 2009. Correlations between dioxin-like and indicators PCBs: potential consequences for environmental studies involving fish or sediment. *Environ Poll* 157, 3451-3456.
- Babut, M., Lopes, C., Pradelle, S., Persat, H., Badot, P.-M., 2012. BSAFs for freshwater fish and derivation of a sediment quality guideline for PCBs in the Rhone basin, France. *Journal of Soils Sed* 12, 241-251.
- Babut, M., Miège, C., Roy, A., Lopes, C., Roux, G., Desmet, M., et al., 2011. Transferts de contaminants hydrophobes du sediment au biote: construction de modèles dans une perspective de gestion (Transfer of hydrophobic contaminants from sediment to biota: construction of models for environmental management). Cemagref report (in French), Lyon, France; 186 p.

- 1
2
3
4 Beck HL, Helfer IK, 1990. Estimates of fallout in the continental U.S. from Nevada weapons
5
6 testing based on gummed-film monitoring data. *Health Phys* 59, 565–76.
7
8
9 Blott, S.J., Pye, K., 2001. GRADISTAT: a grain size distribution and statistics package for the
10
11 analysis of unconsolidated sediments. *Earth Surface Proc Landforms* 26, 1237-1248.
12
13
14 Breivik, K., Sweetman, A., Pacyna, J.M., Jones, K.C., 2002. Towards a global historical emission
15
16 inventory of selected PCB congeners -- a mass balance approach 2. Emissions. *Sci Total*
17
18 *Environ* 290, 199-224.
19
20
21
22 Brodhag, C., 1989. PCB livre blanc, ou le Pyralène dans tous ses états Commission
23
24 environnement des Vers, 104 p.
25
26
27 Chevreuil, M., Blanchard, M., Teil, M.J., Chesterikoff, A., 1988. Polychlorobiphenyl behavior in
28
29 the water/sediment system of the Seine River, France. *Water Research* 32, 1204-1212.
30
31
32
33 Desmet, M., Mourier, B., Mahler, B.J., Van Metre, P.C., Roux, G., Persat, H., Lefèvre, I., Peretti,
34
35 A., Chapron, E., Simonneau, A., Miege, C., Babut, M., 2012. Spatial and temporal trends in
36
37 PCBs in sediment along the lower Rhône River, France. *Sci Total Environ* 433, 189-97.
38
39
40 Dmitruk, U., Piašcik, M., Taboryska, B., Dojlido, J., 2008. Persistent organic pollutants (POPs) in
41
42 bottom sediments of the Vistula river, Poland. *Clean – Soil, Air, Water* 36, 222-229.
43
44
45
46 Eaufrance, 2011. L'eau dans le bassin Rhône-Méditerranée. [http://www.rhone-](http://www.rhone-mediterranee.eaufrance.fr/usages-et-pressions/pollution_PCB)
47
48 [mediterranee.eaufrance.fr/usages-et-pressions/pollution_PCB](http://www.rhone-mediterranee.eaufrance.fr/usages-et-pressions/pollution_PCB), accessed July 12, 2011.
49
50
51 Eisenreich, S.J., Capel, P.D., Robbins, J.A., Boubonniere, R.A. 1989. Accumulation and diagenesis
52
53 of chlorinated hydrocarbons in lacustrine sediments. *Environ Sci Technol* 23, 1116-26.
54
55
56 European Commission, 2011. Commission Regulation (EU) No 1259/2011 of 2 December 2011
57
58 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like
59
60
61
62
63
64
65

1
2
3
4 PCBs and non dioxin-like PCBs in foodstuffs. In: European Commission, editor. 1259/2011, 6
5
6
7 p.

8
9 Groupement d'Études Méthodologiques pour l'Analyse des Sols; 2011.

10
11 <http://www.gemas.asso.fr/?documentation=normalisation1>, accessed July 13, 2011.

12
13
14 Hammond, P.B., Nisbet, I.C.T., Sarofim, A.F., Drury, W.H., Nelson, N, and Rall, D.P., 1972. PCBs
15
16
17 environmental impact. *Envir Res.* 5, 249-362.

18
19 Heath, E., Ščančar, J., Zuliani, T., Milačič, R., 2010. A complex investigation of the extent of
20
21
22 pollution in sediments of the Sava River: Part 2: Persistent organic pollutants. *Environ*
23
24
25 *Monitor Assess* 163, 277-293.

26
27 Kachigan, S.K., 1991. *Multivariate Statistical Analysis*. Radius Press, NY.

28
29
30 Lecce, S.A., Pavlowsky, R.T., 1997. Storage of mining-related zinc in floodplain sediments, Blue
31
32
33 River, Wisconsin. *Physical Geography*, 18, 424-439.

34
35 Lopes, C., Perga, M.E., Roy, A., Roger, M.C., Persat, H., Babut, M., 2011. Is PCBs concentration
36
37
38 variability between and within freshwater fish species explained by their contamination
39
40
41 pathways? *Chemosphere* 2011, 85, 502-508.

42
43 Martin-Fernandez, J.A., Barcelo-Vidal, C., Pawlowsky-Glahn, V., 1998. Measures of difference for
44
45
46 compositional data and hierarchical clustering methods, in A. Buccianti, G. Nardi, and R.
47
48 Potenza, eds., *Proceedings of IAMG'98, The Fourth Annual conference of the International*
49
50
51 *Association for Mathematical Geology: De Frede, Naples*, p. 526–531.

52
53 Pinglot, J.F., Pourchet, M., 1995. Radioactivity measurements applied to glaciers and lake
54
55
56 sediments. *Sci Total Environ* 173/174, 211-223.

- 1
2
3
4 Royal Order, 2000. Concerning the maximum dioxin and polychlorinated biphenyl content in
5
6
7 certain foodstuffs. Belgisch Staatsblad 31.0.2000. Brussels: Ministry of Social Services, Public
8
9 Health and Environment, p. 18791.
10
11
12 Rozan, T.F., Hunter, K.S., 2001. Effects of discharge on silver loading and transport in the
13
14 Quinnipiac River, Connecticut. *Sci Total Environ* 279,195-205.
15
16
17 Santiago, S., Thomas, R.L., Larbaigt, G., Corvi, C., Rossel, D., Tarradellas, J., et al., 1994. Nutrient,
18
19 heavy metal and organic pollutant composition of suspended and bed sediments in the
20
21 Rhone River. *Aquatic Sci* 56, 220-42.
22
23
24
25 Thió-Henestrosa, S., Martín-Fernández, J.A., 2005. Dealing with compositional data: the
26
27 freeware CoDaPack. *Mathematical Geology* 37, 773-793.
28
29
30 Van Metre, P.C., Callender, E., Fuller, C.C., 1997. Historical trends in organochlorine compounds
31
32 in river basins identified using sediment cores from reservoirs. *Environ Sci Technol* 31, 2339-
33
34 44.
35
36
37
38 Van Metre, P.C., Mahler, B.J., 2005. Trends in hydrophobic organic contaminants in lake
39
40 sediment across the United States, 1970-2001. *Environ Sci Technol* 39, 5567-74.
41
42
43 Van Metre, P.C., Wilson, J.T., Callender, E., Fuller, C.C., 1998. Similar rates of decrease of
44
45 persistent, hydrophobic contaminants in riverine systems. *Environ Sci Technol* 32, 3312-17.
46
47
48 Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in World
49
50 Rivers: New insights from a new database. *Sci Total Environ* 407, 853-868.
51
52
53 Viganò, L., Roscioli, C., Erratico, C., Guzzella, L., 2008. Polybrominated diphenyl ethers (PBDEs)
54
55 and polychlorinated biphenyls (PCBs) in 0+ juvenile cyprinids and sediments of the Po River.
56
57 Arch. Environ. Contamin. Toxicol. 55, 282-294.
58
59
60
61

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Ward, J.H., Jr. 1963. Hierarchical grouping to optimize an objective function. J. American
Statistical Assoc. 58, 236-244.

1
2
3
4 **Figure captions**
5
6
7

8 **Figure 1** Map of the study area (Rhône River basin, France) and locations of sediment core
9 collection.
10

11
12
13
14 **Figure 2** Proportions of the seven indicator PCB congeners for centroids of five clusters.
15
16
17

18 **Figure 3** Profiles of the sum of the concentrations of the seven indicator PCBs (ΣPCB_i) in
19 sediment cores collected from the Rhône River basin, France. The color of each symbol
20 corresponds to its PCB congener assemblage cluster (fig. 2).
21
22
23
24

25 **Figure 4.** (A) Median ΣPCB_i concentrations in sediment core samples for decadal time windows.
26 Site GDL is excluded because sediment at this site was disturbed by reservoir management
27 activities. Two-parameter exponential models were fit to the 1986–95, 1996–2005, and post-
28 2005 time windows (adjusted r^2 of 0.92, 0.96, and 0.94, respectively). Data for the 1967–75 and
29 1976–85 time windows were not modelled as insufficient data were available for many of the
30 sites. Arrows indicate sediment benchmarks calculated from BSAFs models that correspond to
31 PCB thresholds in fish (Lopes et al., 2011; Babut et al., 2012). (B) Cumulative population in the
32 catchment upstream of each sampling site. Census data from L'Institut national de la
33 statistique et des études économiques (INSEE)
34 (http://www.insee.fr/fr/themes/detail.asp?reg_id=99&ref_id=base-cc-evol-struct-pop-2010).
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 1 Characteristics of sediment-core collection sites and sediment cores.

Site name (abbreviation)	Fluvial setting	X (Latitude)	Y (Longitude)	Distance from the outlet of Lake Geneva (km)	Core ID	Core length (cm)
Gravière des Etournels (ETL)	Former quarry	5.935603	46.131889	23	ETL 10-02	98
La Morte (MTE)	Secondary channel	5.554050	45.701586	104	MTE 08-03	69
Grand Large (GDL)	Reservoir	4.972078	45.778453	171	GDL 09-07	55
Crépieux (CPX)	Former quarry	4.916314	45.803050	175	CPX 08-01 CPX 08-02	78 94
Table Ronde (TBR)	Small embayment on the right bank	4.799633	45.610754	197	TBR 09-01	123
Ile du Beurre (BRE)	Secondary channel	4.782072	45.476389	222	BRE 08-01 BRE 08-03	106 98
Arras (ARS)	Off-channel basin	4.807308	45.132542	263	ARS 10-02	135
Lône de la Grange Ecrasée (GEC)	Secondary channel	4.655806	44.390028	354	GEC 11-04	100

Figure 1

[Click here to download Figure 1 APPROVED.pdf](#)

Author produced version of the article published in Science of the Total Environment (2014), vol. 476-477, p. 568-576
The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

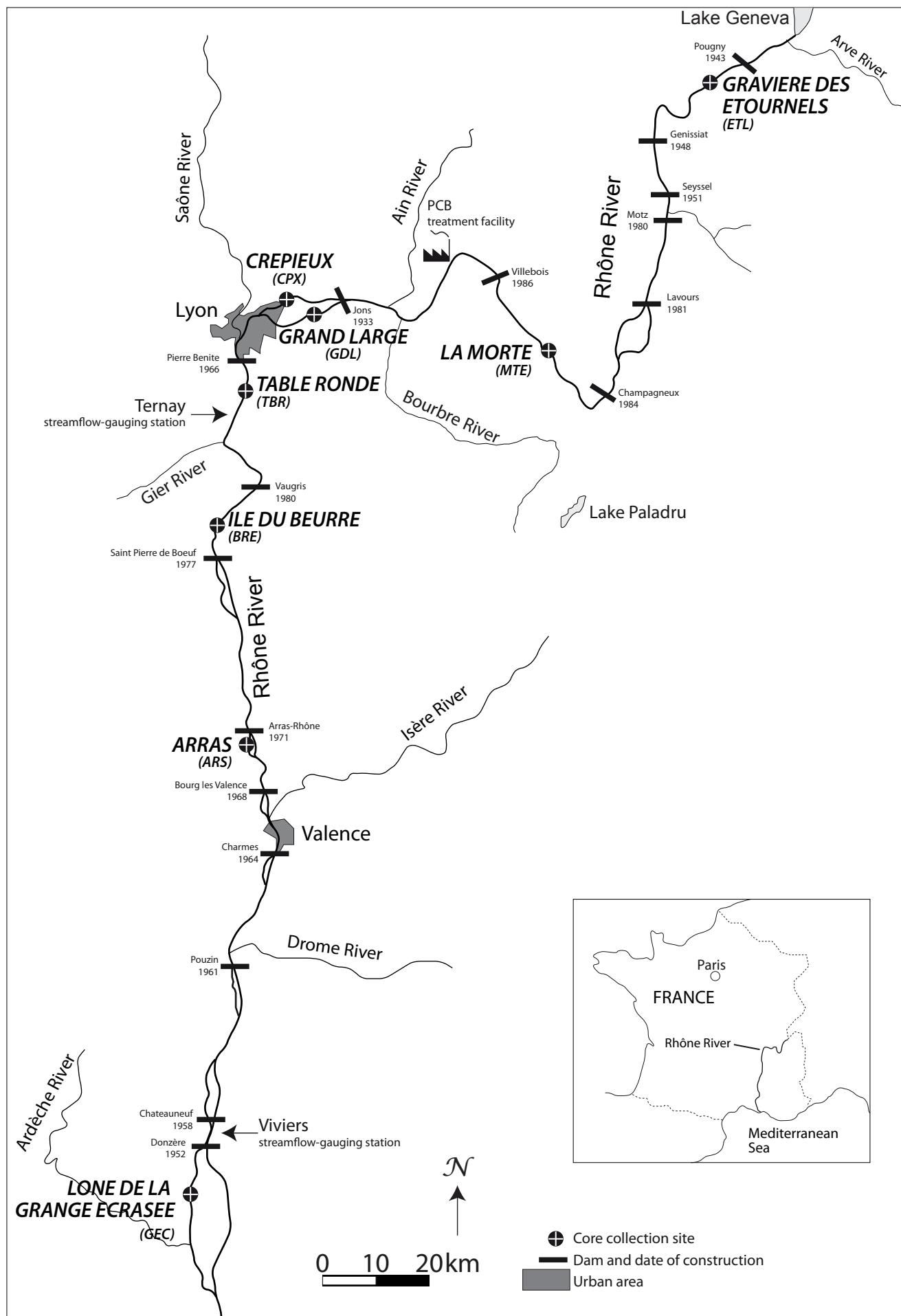


Figure 1

Figure 2

[Click here to download Figure: Fig 2 APPROVED.pdf](#)

Article produced version of the article published in Science of the Total Environment (2014), vol. 476-477, p. 568-576
The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

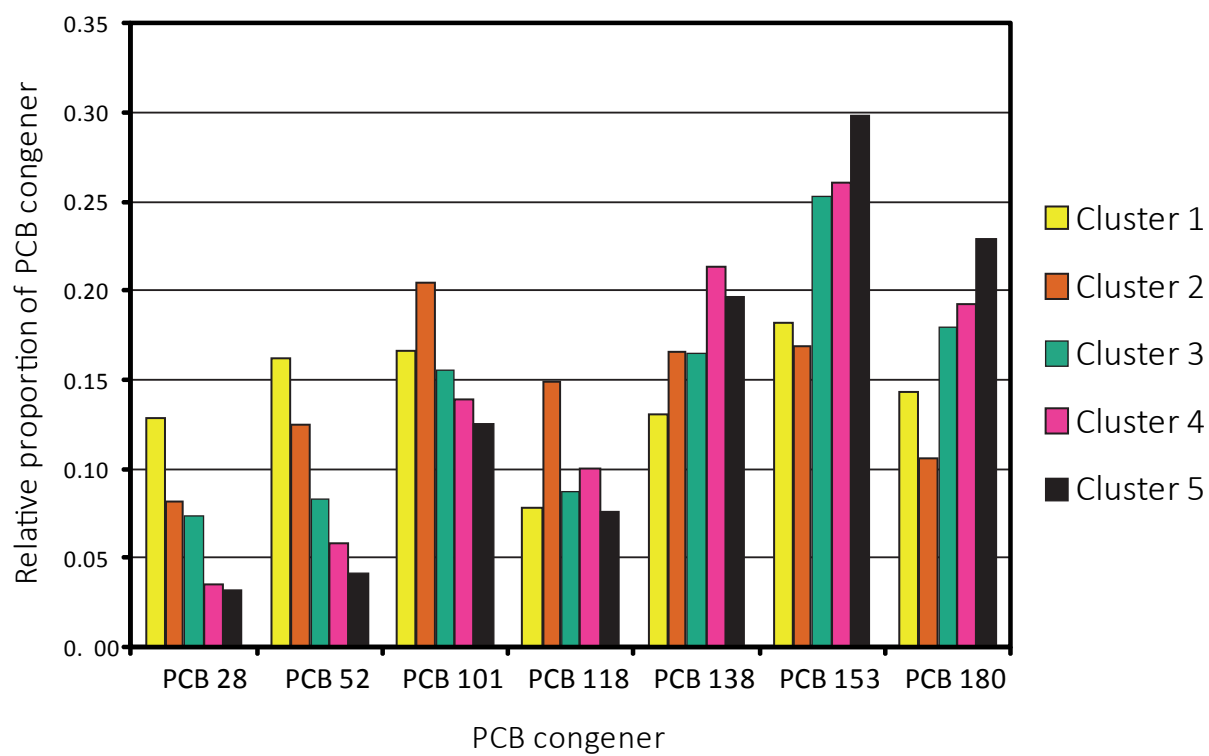


Figure 2

Figure 3

[Click here to download Figure: Fig 3 APPROVED.pdf](#)

Author-produced version of the article published in Science of the Total Environment (2014), vol. 476-477, p. 568-576
The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

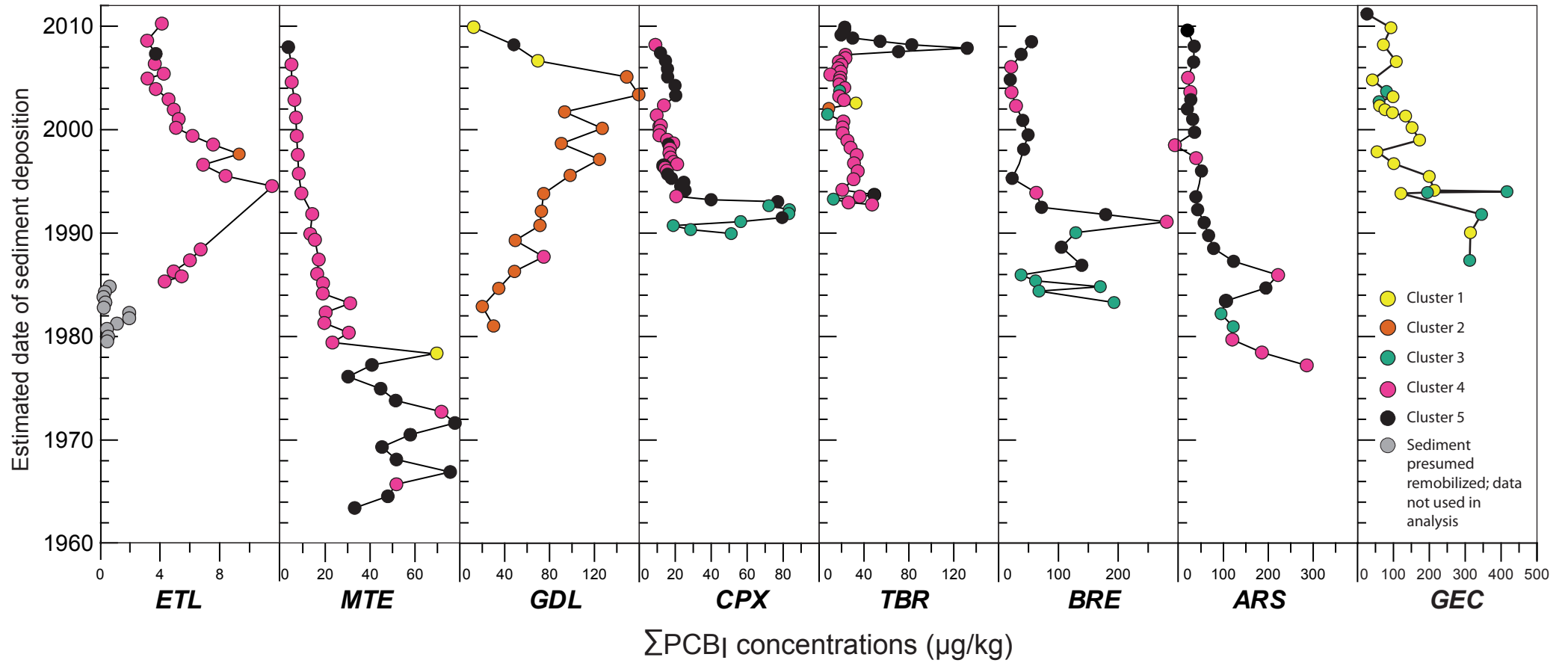


Figure 3

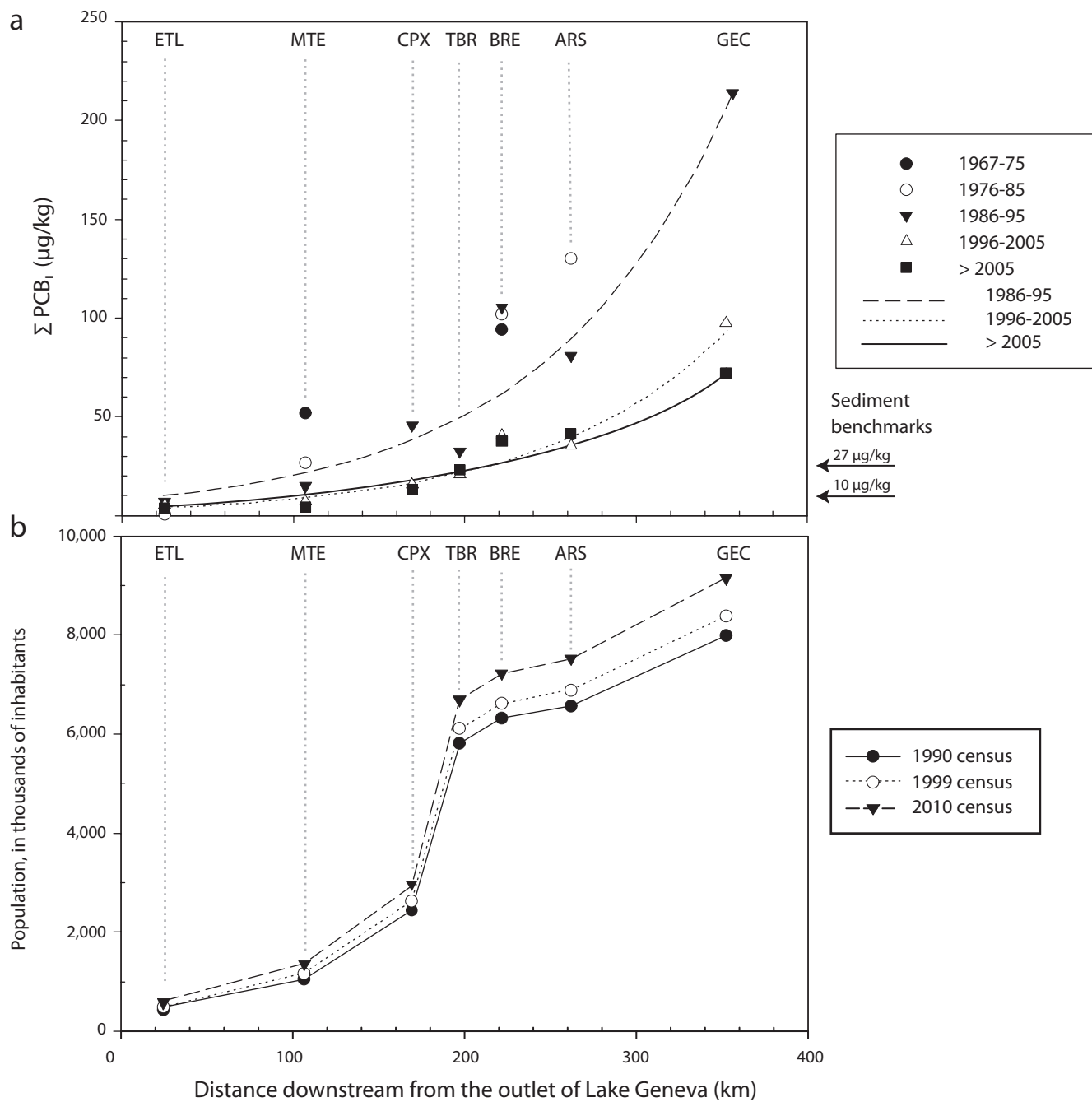


Figure 4

Supplementary Figures

[Click here to download Supplementary material for online publication only: Supplementary information APPROVED.pdf](#)

The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

Supplementary Table

[Click here to download Supplementary material for online publication only: Supplementary Table S1 APPROVED.xls](#)

The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

KML File (for GoogleMaps)

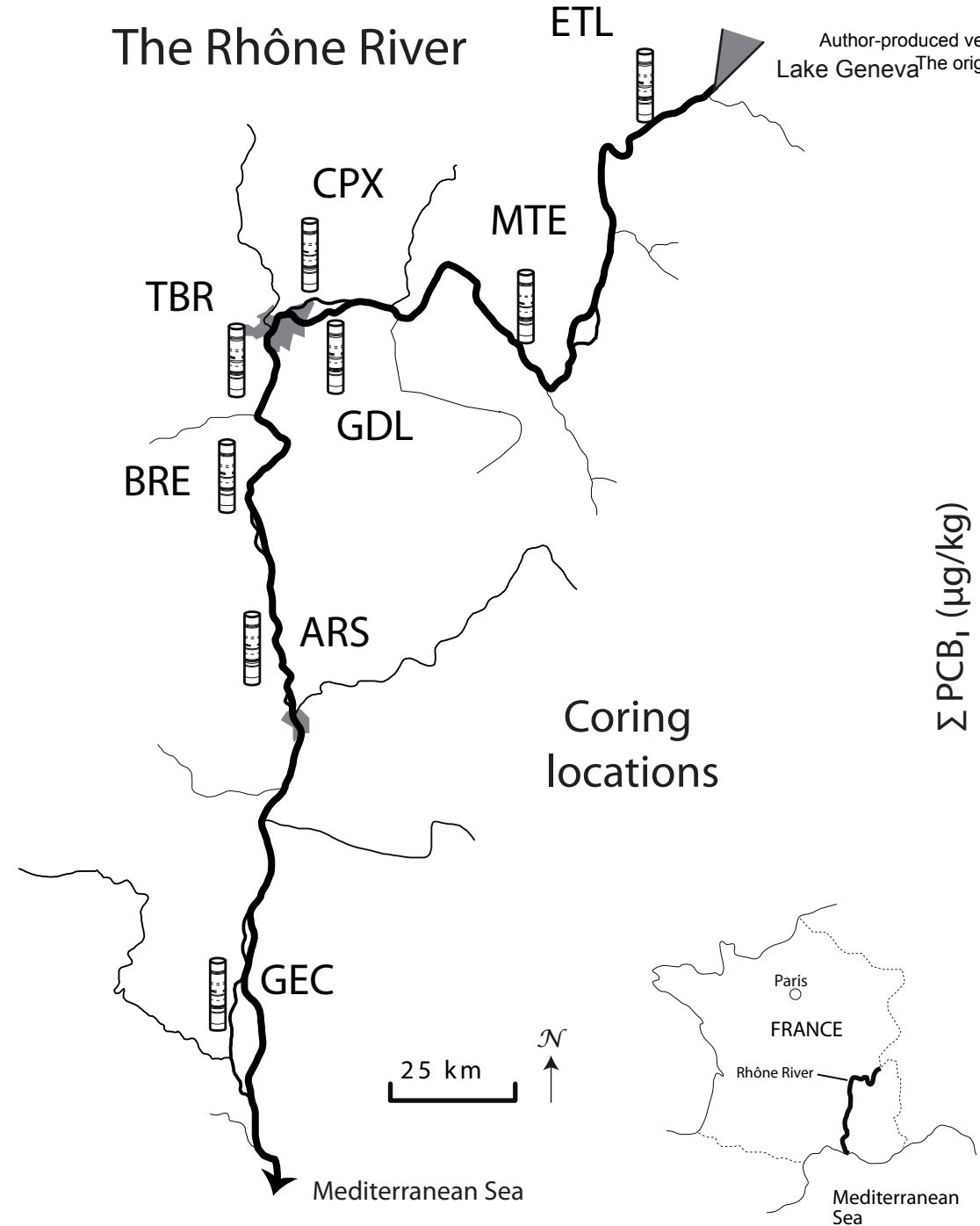
[Click here to download KML File \(for GoogleMaps\): Rhom-Cores_ENTPE.kml](#)

Author produced version of the article published in Science of the Total Environment (2014), vol. 476-477, p. 568-576

The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

Conflict of interest

We declare no conflict of interest. Funding agencies had no role in the study design; in the collection, analysis, or interpretation of data; in the writing of the report; nor in the decision to submit the article for publication.



Author-produced version of the article published in Science of the Total Environment (2014), vol. 476-477, p. 568-576
The original publication is available at <http://www.sciencedirect.com/> doi : 10.1016/j.scitotenv.2014.01.026

Spatial trends for PCBs for decadal time windows

