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## Recent Applications of Flame Atomic Absorption Spectrometry to Environmental Measurements

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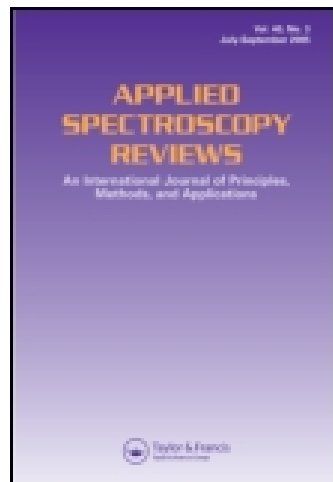
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## Applied Spectroscopy Reviews

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/laps20>

### RECENT APPLICATIONS OF FLAME ATOMIC ABSORPTION SPECTROMETRY TO ENVIRONMENTAL MEASUREMENTS

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Published online: 27 Oct 2011.

To cite this article: Michael A. Janusa & James N. Beck (2002) RECENT APPLICATIONS OF FLAME ATOMIC ABSORPTION SPECTROMETRY TO ENVIRONMENTAL MEASUREMENTS, Applied Spectroscopy Reviews, 37:2, 137-186, DOI: [10.1081/ASR-120006043](https://doi.org/10.1081/ASR-120006043)

To link to this article: <http://dx.doi.org/10.1081/ASR-120006043>

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## RECENT APPLICATIONS OF FLAME ATOMIC ABSORPTION SPECTROMETRY TO ENVIRONMENTAL MEASUREMENTS

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### ABSTRACT

Atomic absorption spectroscopy is very useful for the determination of a large number of elements, especially at trace levels. It is a widely used technique for analysis of a wide variety of sample matrices including biota, soils, and water. Atomic absorption spectroscopy is a very reputable technique that is inexpensive and delivers accurate results even in a complex matrix. This review focuses on the applications of flame atomic absorption spectroscopy to environmental measurements, and is mainly based on papers published from 1999–2002.

*Key Words:* Flame atomic absorption; Elemental analysis; Literature review; Sediments; Water; Biota; Methods

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## I. INTRODUCTION

Most compounds break apart into atoms in the gaseous phase when heated to a sufficiently high temperature. The spectra of these atoms consist of very sharp lines with each element having its own characteristic spectrum. There is usually little overlap between the spectra of different elements in the same sample due to the sharpness of these lines. Atomic absorption spectrometry (AAS) takes advantage of this phenomenon and is based on neutral or ground state atoms of an element absorbing electromagnetic radiation over a series of very narrow wavelengths. In AAS, samples are vaporized at very high temperatures and the concentrations of selected atoms are determined by measuring absorption at their characteristic wavelengths. This is typically accomplished by converting the sample into an atomic vapor by spraying a solution into a flame.

Atomic absorption spectrometry is a rapid and relatively inexpensive method for the determination of metal concentrations in a wide variety of samples. This elemental analysis technique was discovered in the early 1950s.<sup>[1,2]</sup> It has grown over the years into a well-used and widely accepted technique for trace metal determination that is almost independent of the molecular form of the metal in the sample. This method is very sensitive and

can detect different metals (70–80 elements) in concentrations as low as and frequently lower than 1 ppm. Atomic absorption spectrometry has become one of the principal tools of analytical chemistry because of the high sensitivity and ease with which many samples can be analyzed. Typically, the sample is diluted to reduce concentrations to the ppm level to analyze the major constituents of an unknown.

One of AAS's advantages is that determinations can be made in the presence of other elements; however, this is also a disadvantage because only one element can be analyzed at a time. The technique requires a different light source (hollow-cathode lamp) and wavelength for each element being analyzed. When less than four different metals are to be determined, AAE is frequently the choice of the analyst. If more than four different metals are to be determined, inductively coupled plasma-atomic emission spectrometry (ICP-AES) or more recent inductively coupled plasma-mass spectrometry (ICP-MS) has become the technique of choice. Atomic absorption spectrometry also has the limitations of being incapable of distinguishing among oxidation states/chemical environments of the analyte elements and being insensitive to nonmetallic elements. An advantage for AAS over the other instruments is cost. A typical AAS can be purchased between \$10,000–\$35,000 which is much less expensive than the ICP-AES or ICP-MS. The total market for AAS for 1998 was estimated at approximately \$317 million. AAS has the reputation as a technique that works and is capable of analyzing several different metals in a complex matrix.

This review focuses on the applications of AAS to analyze samples that include biota, soils, water, and new methods of preconcentrating metals in water samples prior to making AAS measurements. A brief overview of the basic principles and instrumentation used in AAS is described. Background material on the discovery and history of AAS is given elsewhere.<sup>[3]</sup>

## II. BASIC PRINCIPLES

Light of a specific wavelength will impinge on previously generated ground state atoms. The atoms absorb this light and a transition to a higher energy level will occur. The intensity of this transition is related to the concentration of the ground atoms, and can be represented as follows:

$$T = \frac{P}{P_0} \quad (1)$$

Where  $T$  is the transmittance,  $P$  is the power of the light source passing through the sample zone, and  $P_0$  is the power of the light source after it has passed through the sample zone. The sample zone of path length,  $b$ , is relatively long to maximize the amount of light absorbed by the atoms. The amount of light absorbed is dependent on the atomic absorption coefficient,  $k$ . This value is related to the number of atoms/m<sup>3</sup> in the atom cell,  $n$ ; the Einstein probability for the absorption process and the energy difference between the two levels of the transition. In practice, these are all constants that can be combined to give one constant, called the absorptivity,  $a$ . The value  $k$  is related exponentially to the transmittance as follows:

$$T = \frac{P}{P_0} e^{-kb} \quad (2)$$

In practice, the absorbance,  $A$ , is used in AAS and is related logarithmically to the transmittance as follows:

$$A = -\log T = \log \frac{P_0}{P} = \log \frac{1}{T} = kb \log e = 0.43 kb \quad (3)$$

The Beer–Lambert Law relates  $A$  to the concentration of a metal in the atom cell,  $c$ , as follows:

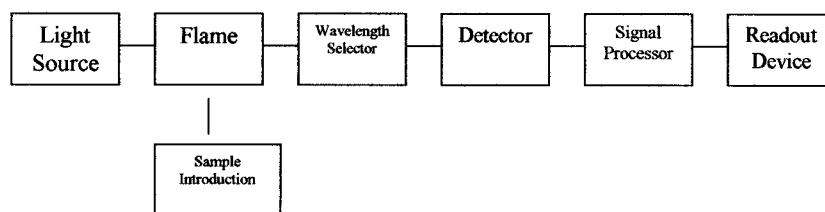
$$A = abc \text{ or } \epsilon bc \quad (4)$$

where  $a$  is the absorptivity in g/lcm,  $\epsilon$  is the molar absorptivity mol/lcm, and  $b$  is the cell length in centimeters.

### III. INSTRUMENTATION

A detailed description of instrumentation for AAS is available elsewhere.<sup>[4]</sup> Current instrumentation combines all the components briefly described here into a compact bench type unit for the user. A schematic diagram of a typical flame atomic absorption spectrometer is shown in Figure 1.

The radiation source is almost always a hollow cathode lamp (HCL) or for more volatile metals such as zinc and cadmium an electrodeless discharge lamp (EDL). Its function is to provide light of a very specific wavelength with a width of approximately 0.2 nm. A separate lamp is needed for each metal of interest although some multi-metal lamps for two or three metals are available. The atom cell used to determine the presence of an element is the flame with the air–acetylene flame the most widely used. For refractory metals such as molybdenum, the hotter



*Figure 1.* Schematic diagram of flame AAS.

$\text{N}_2\text{O}$ -acetylene flame is recommended. The object of the flame is to create ground state atoms. The sample is introduced in an aqueous form through a pneumatic nebulizer. Various other sample introduction systems have been proposed, often for a particular sample need.<sup>[5]</sup> The monochromator will isolate the wavelength (radiation) of interest from other wavelengths, and has a typical resolution of 0.02–2 nm. The detection system is most frequently a photomultiplier tube (PMT). Its basic function is to convert a light signal into an electrical signal. Recent work has used the photodiode array (PDA) or charge transfer devices (CTDs). Readout devices were originally meters with calibrated scales. Modern instrumentation has digital displays or graphic presentations on video units or external computers. Hard copy can be provided. In practice AAS usually has a fast electronics capability and most commercial systems have interchangeable flame and furnace.<sup>[6]</sup>

The unique properties of mercury have led to the development of cold vapor-AAS as the most widely used method of analysis. Elemental mercury exhibits an appreciable vapor pressure, even at room temperature and the vapor is mono-atomic. This results in no need for the flame provided mercury in the sample could be converted into its elemental form. A detailed description of this technique is presented elsewhere.<sup>[7,8]</sup>

#### IV. PRACTICE OF ATOMIC ABSORPTION SPECTROMETRY

AAS in common with many analytical techniques is not an absolute method of analysis. A comparison with standards (usually aqueous) is the most common method for performing quantitative analysis. A calibration curve is established with (usually) four standards and a blank. The unknown sample can be compared to the calibration curve and its concentration established. The unknown concentration should be higher than the lowest

standard and lower than the highest standard. If the signal is higher than the lowest standard then a dilution is recommended. If the unknown signal is lower than the lowest standard then preconcentration or another technique is recommended. Linearity of the calibration curve in AAS is (typically) 2–3 orders above the detection limit. Most analyses are performed on samples, which have a more complex matrix than the aqueous standards, in this case the use of matrix matched standards or standard-additions is recommended.<sup>[4]</sup> Accuracy can be established using a comparison to a different method or more commonly by comparison to a standard reference material. There are numerous agencies around the world, which produce standard reference materials with NIST (National Institutes of Standards & Technology, Gaithersburg, MD, USA) being the most widely used. Flame AAS is an ideal technique when the concentration of the metal in the sample is around one ppm or higher and at least several milliliters of sample are available.

#### V. RECENT DEVELOPMENTS IN ATOMIC ABSORPTION SPECTROMETRY

For the most part, AAS has seen few major changes in the last two decades. In the late 1980s/early 1990s several commercial multimetal systems became available, typically 4–6 metals on a simultaneous basis.<sup>[9]</sup> These systems did not attract as much interest because of the ready availability of ICP-AES. Improvements in software, computer control, and data reduction were developed for AAS as for all other atomic spectroscopic techniques. Recent interest in the chemical form or speciation of a metal has led to the development of hybrid techniques involving separation methods (chromatography, electrophoresis, etc.) and AAS,<sup>[10]</sup> as well as flow injection analysis.<sup>[11]</sup> A major reason that few major developments have occurred in AAS in the last few decades is because it has matured as an analytical technique and for many applications ‘it works’.

There is atomic absorption spectroscopy instrumentation available that allows field analysis to be conducted. The advantage of field chemistry is reduction of analysis time and cost by providing analytical data on site while eliminating the need for sample collection and transport. The areas of environmental monitoring and industrial process control are two of the prime candidates for this type of technique. One version of a portable atomic absorption spectrometer is the W Coil AAS.<sup>[12]</sup> It best meets the criteria needed in the design of an inexpensive, portable, electrothermal atomic absorption spectrometer. It has the sensitivity of a graphite furnace. The system uses a thin metal wire instead of a graphite furnace, which



results in the need for low current and voltage to electrically heat the filament.<sup>[13,14]</sup> This results in an inexpensive, compact, battery-powered tungsten coil atomizer. The availability of inexpensive, compact, fast, linear charge-coupled device detectors have made the portable atomic absorption spectrometer a reality.<sup>[15]</sup> A detailed description of this technique and comparative results between flame, graphite furnace, and W coil atomic absorption spectroscopy is presented elsewhere.<sup>[12]</sup>

## VI. RECENT APPLICATIONS IN ATOMIC ABSORPTION SPECTROMETRY

### A. Monitoring Studies in Sediments

Atomic absorption has been used for the analysis of many elements in sediment samples from surficial to segments extracted from cores. Applications encompassed quantitative elemental measurements in a wide range of soil and sediment samples to monitor changes in sediment loads and to determine the geochemical processes that alter the chemical species of each element. Samples are typically extracted and analyzed using many different extraction procedures. This section summarizes published literature during the past three years and current methods of analysis of sediment and soil and results of that analysis. This manuscript focuses on the use of flame atomic absorption or cold vapor method for Hg and does not attempt to review all atomic absorption techniques. In many cases, the development of newer technology leads to the abandonment of older technology such as the use of flame atomic absorption, but this technique will continue to play an important role in elemental analysis, mainly because of equipment cost, cost of analysis, ease of analysis, and mainly because it works.

Gauthreaux et al.<sup>[16]</sup> studied the effect of using possibly metal contaminated sediments (dredge spoils) to restore marsh at Sabine National Wildlife Refuge in southwestern Louisiana, USA. The authors made use of the Tessier<sup>[17]</sup> sequential extraction procedure to separate the chemical species of the metals Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The metals were separated into the operationally defined fractions exchangeable, carbonates, iron/manganese oxides, organics, and residual phases. Table 1 gives a comparison of summed fractions from the sequential extraction procedure, with results from mean metal concentrations for previous studies in the same general area. With the exception of increases in Mn, no other metals were elevated at the sampling sites in the study area. The sequential extraction procedure was found to yield reproducible and reliable results that were found statistically significant.

**Table 1.** Comparison of Summed Fractions, Total Digestion, and Means for Results of Previous Investigations on Cr, Cu, Fe, Mn, Ni, Pb, and Zn for Calcasieu Ship Channel Sediments. Reprinted from Gauthreaux et al.<sup>[16]</sup> by Permission of the Authors

Metal	Summed Fraction (ppm)	Total Digestion (ppm)	Previous Studies (ppm)
Cr	28.4	31.1	27.0
Cu	7.6	8.0	15.0
Fe	8,700	9,000	14,800
Mn	998	978	630
Ni	11.8	12.9	13.0
Pb	5.5	5.4	13.0
Zn	30.6	36.9	53.0

Kwon and Lee<sup>[18]</sup> studied the effect of wastewater discharge into Masan Bay, Korea. Sewage plants located at Masan City and Changwon city have been suggested as the main source of trace metals Cr, Cu, Fe, Pb, and Zn to the bay. They used the sequential extraction procedure of Tessier<sup>[17]</sup> to separate the metals into different geochemical phases. The exchangeable fraction of surficial sediments were found to contain the following percentages of total metal in sediment: Zn 35.0%, Pb 5.3%, Cu 0.86%, Cr 0.01%, and Fe 0%. Deeper sediments were found to have higher percentages of metals in the residual phase and a decrease in the bioavailable phases. The effect of metal concentrations found in the exchangeable phases was associated with the potential to cause adverse biological effects. The potential to cause adverse biological effects in sediments were estimated as Zn 69.8%, Pb 35.8%, Cu 29.1%, and Cr 21.1%. Bioconcentration factors were estimated for each metal for crab, oysters, and mullet. Weisz et al.<sup>[19]</sup> collected sediments in rivers and harbors around Lake Balaton and its catchment areas in Hungary. They also used the extraction method of Tessier<sup>[17]</sup> to determine the distribution of As, Cr, Cu, Mn, Ni, Pb, and Zn in the top 10 cm of sediments. Concentrations of studied elements were found mainly below the Hungarian standards set for sediments and geochemical background values. The sequential extraction procedure revealed that most elements were located in the acid-soluble residue and bound to organic matter/sulfide fraction. They reported that Pb and Cu were found in higher concentration in and around harbors when concentrations were compared to small rivers. The pollution was thus found to be highly localized and had not migrated to the lake.

Gauthreaux et al.<sup>[20]</sup> measured the heavy metals Cr, Cu, Fe, Mn, Ni, Pb, and Zn in restored marsh sediments collected from the Sabine National Wildlife Refuge in southwestern LA, USA. These metals were selected due to their presence in soils, possible presence in oil from spills, use as micronutrients for plants, or contaminants in biota. The sequential extraction procedure of Tessier<sup>[17]</sup> was used to partition the heavy metals into five operationally defined chemical species containing the metals. The results were examined by the statistical tests MANOVA to see if selected groupings of sampling stations could be distinguished by metal concentration, ANOVA determined the metals that were causing the effect observed by the MANOVA, and then by discriminant analysis using Duncan's multiple range test. Results presented as Table 2 show that the metal data can be used to correctly identify the station where the results originated from 92.2% of the time. Table 3 gives the mean concentrations of the studied metals for each of the sampling stations.

The results vary significantly between stations, particularly for Fe and Mn. The Tessier<sup>[17]</sup> method can yield accurate results as shown in Table 4, when summed data for the sequential extraction procedure is compared to mean concentrations found in subsamples that were extracted using microwave digestion techniques. The agreement is gratifying. Table 5 gives the summed concentrations (mg/kg) of studied metals in subsamples extracted by the sequential extraction procedure compared to concentrations in totally digested samples, as measured by previously studies done near the Sabine National Wildlife Refuge study area. Agreement between the data sets is quite good and shows the reliability and reproducibility of the extraction procedures.

**Table 2.** Discriminant Analysis of Metal Data Classifying Metal Concentrations in Each Station Grouping. Reprinted from Gauthreaux et al.<sup>[20]</sup> by Permission of the Authors

Actual Groups	No. of Cases	Predicted Group Membership <sup>a</sup>		
		1	2	3
1	45	38	5	2
		85.0%	10.5%	4.5%
2	105	2	95	8
		18.5%	90.6%	7.6%
3	133	0	10	123
		0.0%	7.8%	92.2%

<sup>a</sup>Percent of group cases correctly classified were 91.22%.

**Table 3.** Mean Metal Concentrations and Standard Deviations by Sampling Site in ppm Unless Noted. Numbers in Parentheses are the Number of Samples Used in Calculating Means. Reprinted from Gauthreaux et al.<sup>[20]</sup> by Permission of the Authors

Site	Cr	Cu	Fe (%)	Mn	Ni	Pb	Zn
I	18.5 (6) ± 2.0	11.0 (6) ± 3.1	1.82 (6) ± 0.61	210 (6) ± 90	20.4 (6) ± 2.5	6.4 (5) ± 0.7	47.1 (6) ± 5.4
II	21.8 (22) ± 2.9	14.5 (11) ± 6.2	1.95 (11) ± 0.55	640(22)	19.5 (11) ± 3.0	8.3 (9) ± 0.9	55.5 (22) ± 11.5
III (before)	19.5 (6) ± 2.5	10.0 (6) ± 3.5	0.41 (6) ± 0.22	151 (6) ± 30	10.4 (6) ± 2.8	6.8 (4) ± 0.8	36.5 (6) ± 4.1
III (after)	18.1 (6) ± 3.8	13.6 (6) ± 1.8	1.91 (3) ± 0.35	648 (6) ± 145	12.1 (3) ± 3.2	5.6 (2) ± 0.4	41.0 (6) ± 8.1
IV	23.6 (14) ± 1.8	10.6 (4) ± 2.7	0.35 (4) ± 0.11	56.2 (3) ± 9.1	17.8 (4) ± 2.5	4.3 (3) ± 0.6	33.0 (4) ± 10.1
V	21.4 (14) ± 4.5	9.9 (14) ± 3.2	2.10 (14) ± 0.61	580 (14) ± 220	14.6 (12) ± 3.5	5.6 (9) ± 0.8	41.6 (14) ± 15.6

**Table 4.** Concentrations (ppm) of Metals in Subsamples Compared to the Concentrations in the Summed Fractions (in Parenthesis) Measured in the Sequential Extraction. Reprinted from Gauthreaux et al.<sup>[20]</sup> with Permission of the Authors

Sample Site	Replicate Number	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
SITE I	In-B	20.1 (21.0)	12.5 (10.6)	19200 (18600)	162 (155)	19.1 (23.2)	6.7 (6.4)	60.6 (54.5)
	Out-A	19.5 (17.4)	11.1 (10.8)	12100 (12500)	104 (94.4)	17.4 (17.3)	7.2 (6.8)	31.9 (32.6)
SITE II	Nonveg-B	24.1 (20.4)	24.9 (23.0)	14600 (16900)	455 (424)	20.7 (19.8)	6.8 (7.1)	55.4 (48.4)
	Veg-C	30.0 (28.2)	20.7 (18.4)	22000 (20300)	709 (688)	21.1 (19.7)	6.4 (6.7)	61.9 (54.4)
SITE III	Prior-A	17.4 (18.2)	8.5 (8.4)	16100 (14000)	128 (122)	16.2 (17.2)	6.4 (6.2)	35.3 (34.2)
	After-A	16.7 (20.8)	16.6 (15.2)	9100 (8700)	591 (589)	14.9 (11.8)	7.2 (5.5)	39.4 (36.0)
SITE IV	In-A	22.4 (22.0)	9.0 (5.0)	2600 (2400)	79.4 (60.8)	10.8 (8.6)	6.7 (6.6)	33.0 (29.2)
	Out-C	30.1 (22.4)	14.9 (12.6)	4100 (3500)	50.8 (43.6)	14.1 (12.4)	5.9 (4.3)	42.7 (37.0)
SITE V	BD-A	31.1 (28.4)	8.0 (7.6)	9000 (8700)	978 (998)	12.9 (11.8)	5.4 (5.5)	36.9 (30.6)
	AD-A	24.7 (19.6)	5.6 (4.8)	7100 (6800)	461 (453)	13.1 (12.8)	5.8 (5.8)	35.4 (38.2)

Hardaway et al.<sup>[21]</sup> restudied a bayou in southwestern Louisiana that contains in its sediments elevated concentrations of the trace metals Cr, Cu, Pb, Hg, and Zn. Samples were digested using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in micro-wavable digestion bombs. They found elevated concentrations of these trace metals at 400 mg/kg Cr, 1100 mg/kg Cu, 10 mg/kg Hg, and 600 mg/kg Pb and Zn. Table 6 shows the concentration of these trace metals at the four sampling stations studied and at four depths in cores taken in the bayou. High concentrations were found where previous studies had found polluted sediments and also found that concentrations agreed with those previously reported. Figure 2 shows the distribution of Cr, Cu, Pb, and Zn with depth in the core and compares the current results with results determined in 1983–1984. It is interesting to note that the current peak concentration is located at greater depth than the previous study. This was interpreted as

**Table 5.** Comparison of Metal Concentrations from Previous Studies with the Current Study on Calcasieu Ship Channel Sediments Taken in the Vicinity of Sabine National Wildlife Refuge. Reprinted from Gauthreaux et al.<sup>[20]</sup> by Permission of the Authors

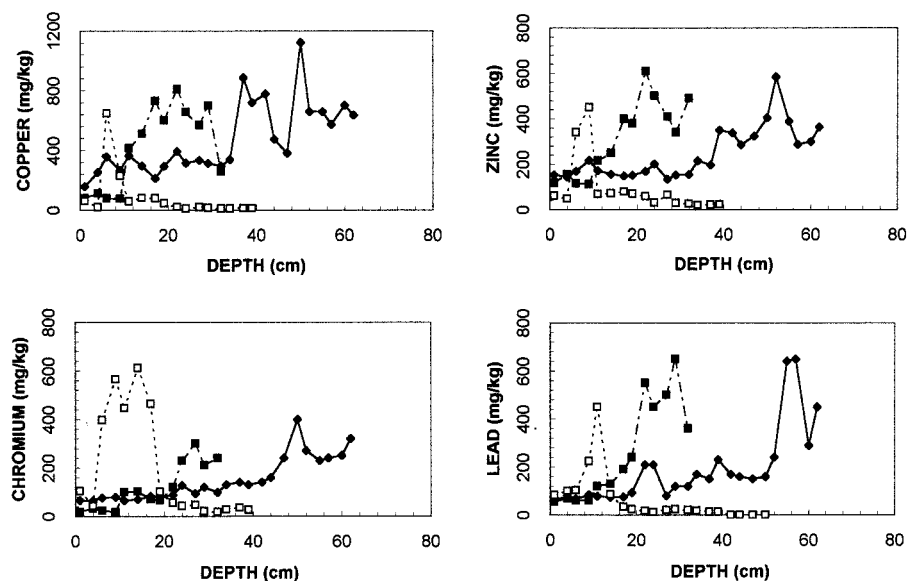
Investigator	Cr (ppm)	Cu (ppm)	Fe (%)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
DeRouen (1986)	19	27	–	–	–	10	45
ICF Kaiser (1989)	25	7	–	–	6	8	36
Cunningham (1990)	28	17	1.97	589	18	8	36
Schultz (1991)	34	15	1.71	670	15	9	84
Army corp. (1993–1994)	10	11	–	–	14	12	36
Wade (1994)	59	8	0.71	–	–	20	61
Sneddon (1995)	17	18	–	–	–	22	70
Mean of all investigators	27	15	1.48	630	13	13	53
Current study means	21	11	2.10	485	15	15	39

**Table 6.** Concentrations of Cr, Cu, Pb, Hg, and Zn Measured in Sediments Collected in Bayou d'Inde, Southwestern Louisiana.<sup>a</sup> Reprinted from Hardaway et al.<sup>[21]</sup> by Permission of the Authors

Station	Depth, cm <sup>b</sup>	Cr, mg/kg	Cu, mg/kg	Pb, mg/kg	Hg, mg/kg	Zn, mg/kg
D0	4	10(9.1)	7.6(7.0)	18(18)	0.06(0.07)	12(14)
	17	12(9.0)	6.9(6.4)	14(20)	0.04(0.04)	15(14)
	29	14(14)	8.0(8.1)	15(16)	0.05(0.03)	17(16)
D1	6	76(70)	360(360)	67(64)	2.2(2.7)	170(160)
	29	98(110)	310(390)	120(140)	1.9(2.0)	150(210)
	50	400(360)	380(390)	160(110)	5.7(6.2)	400(310)
D1A	4	36(36)	120(120)	68(73)	4.3(3.5)	200(210)
	24	45(46)	110(120)	71(68)	3.9(3.5)	180(190)
	37	50(47)	130(130)	69(68)	4.8(4.0)	220(220)
	50	65(62)	150(180)	80(79)	–	210(200)
D1B	6	32(33)	110(110)	89(110)	5.3(4.5)	160(150)

<sup>a</sup>Each value in parenthesis is the concentration measured in a duplicate sediment sample taken from the same sample bag as the original sample.

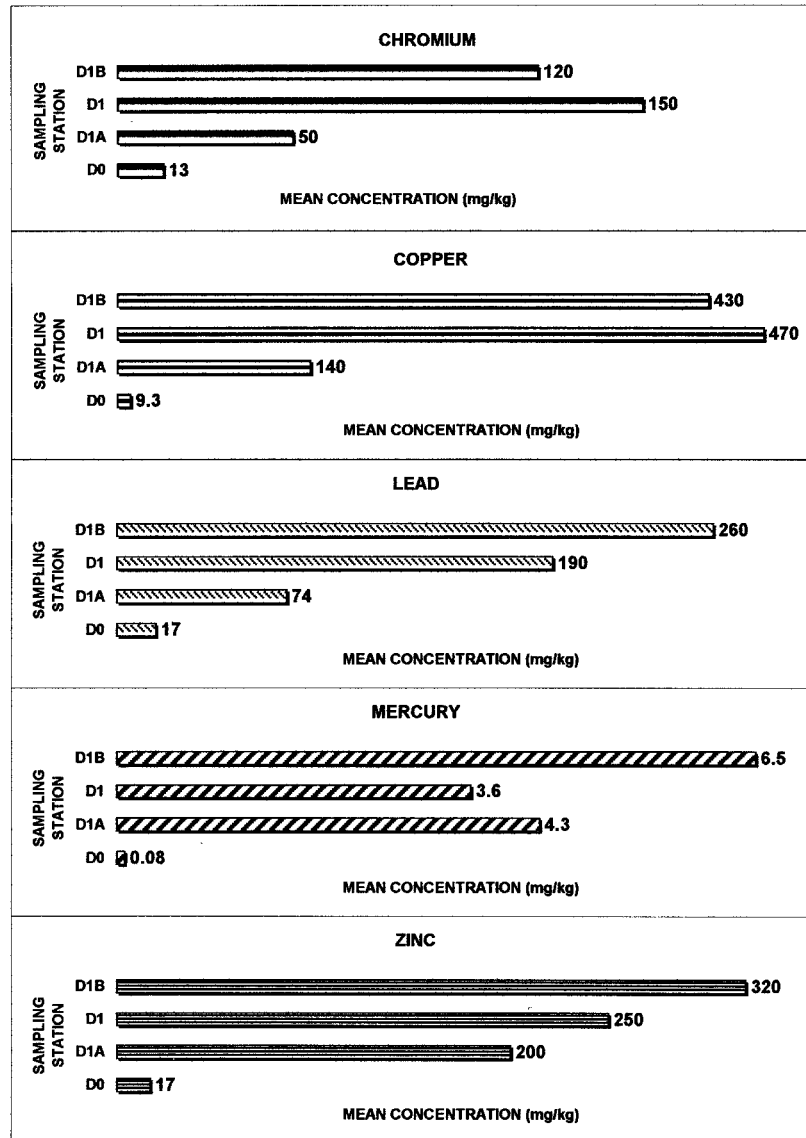
<sup>b</sup>Depth of the core segment analyzed.



**Figure 2.** Variations in concentration (mg/kg) of Cr, Cu, Pb, and Zn with sediment core depth at four sampling stations. The dashed line with open squares represents data collected in 1983–1984 at station D1. The dashed line with closed squares represents sampling station D1B, and the solid line with closed diamonds represents station D1, for samples collected in 1995. Reprinted from Hardaway et al.<sup>[21]</sup> with permission of the authors.

resulting from sedimentation, placing sediment of lower concentration on top of the original sediment peak. Peak concentrations in both studies were similar and remained generally localized within the bayou. Figure 3 shows mean metal concentrations for studied metals at the four sampling stations. Data indicate that metal concentration increases upstream in the bayou. Low concentrations found at the station located at the mouth of the bayou indicate that high concentrations located upstream have not been mobilized and remained localized near the outfall.

Marosits et al.<sup>[22]</sup> have determined the sorption capacity of different soils, including brown forest, carbonaceous sandy, and calcareous chernozjom soils using  $\text{Cu}^{2+}$  as a model ion. One gram of dried soil (< 2 mm grain size) was shaken with 100 mmol/L  $\text{Cu}^{2+}$  and placed in a polyethylene tube. Subsamples were removed every 2 h and the Cu removed was determined. The optimum pH for removing Cu was determined to be in the range 3.5–6, having a dependence on soil type. Other parameters studied were the effect



*Figure 3.* A histogram of mean metal concentrations determined for the entire core collected at each of the four sampling stations (D1B, D1, D1A, and D0) showing the decrease in metal concentration from D1 to the mouth of the bayou. Mean metal concentrations (mg/kg) are given at the right of each bar. Reprinted from Hardaway et al.<sup>[21]</sup> with permission of the authors.



of ion strength and changes in concentration. Ion strength was found to decrease the adsorption capacity, while the presence of large quantities of Na destroyed mineral phases and increased adsorption capacity.

Rácz and Oldal<sup>[23]</sup> investigated the impact of mushrooms on the concentration of the elements Cd, Cs, Hg, Mn, Ni, Pb, and Zn that was added to soil as an amendment. Mushrooms were found to accumulate the metals Cd, Cs, and Hg but did not accumulate Mn. The effect of Mn on the increase in productivity and the pathway for Mn to enter the fruit body was also investigated. Lau et al.<sup>[24]</sup> investigated the analysis of siliceous materials and coal using fusion dissolution for sample decomposition. Concentrations of the oxides, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub>, were measured using an oxalic acid-lithium carbonate-lithium tetraborate (1 : 1 : 1) fusion agent to completely digest the samples. Samples containing > 80% silica were found too difficult to digest due to formation of polysilicic acid precipitates. Quantitative separations of metals could be obtained for 1-g samples of siliceous materials and coal when the silica content was less than 70%. For higher silica contents correction factors were derived to correct for loss of silica through precipitation. Derived correction factors gave corrected concentrations that agreed well with expected concentrations in standard reference materials.

O'Rourke et al.<sup>[25]</sup> measured the concentrations of Hg, using the cold vapor method, in sediments located at Sabine National Wildlife Refuge located in southwestern Louisiana, USA. The study area was the site of a marsh restoration project using dredge spoils from the Calcasieu River. It was known that metal contamination existed north of the study area in sediments and there was a possibility that the contamination had migrated to the vicinity of the study area. Mean concentrations of Hg varied from 0.07 to 0.12 mg/kg across the study area. Table 7 gives the concentration of Hg across the study sites. The samples labeled VEG were sites where restored marsh had revegetated completely after placing dredge spoils there and NON-VEG were areas where the vegetation had not restarted and were felt to be stressed. Mercury concentrations were within acceptable limits for native plants and did not cause die-off of plants.

Kwon et al.<sup>[26]</sup> studied sedimentation patterns and sediment bio-availability of Cu, Fe, and Zn at 41 sites around a wastewater discharge area. They found that discharged pollutants were dispersed to the inner bay and coastline and not to the outer bay and waterway. Fractional composition of Zn in the discharge showed that this metal was present in the exchangeable fraction (239 mg/kg – 35.1%), reducible (163 mg/kg – 24%) carbonates (149 mg/kg – 22%), residual (98 mg/kg – 14.4%), and organics (31 mg/kg – 4.6%). The order changed at depths of 15 cm in the cores taken (residual > reducible > organic > carbonate > exchangeable). Copper

**Table 7.** Concentrations of Mercury (mg/kg) in Sediment and Soil Samples Collected at the Sabine National Wildlife Refuge Marsh Reclamation Site. Reprinted from O'Rourke et al.<sup>[25]</sup> by Permission of the Authors

Sampling Station	Subsamples			Mean	S.D.
	A	B	C		
Site I					
IN	0.10	0.11	0.07	0.09	0.02
OUT	0.08	0.08	0.06	0.07	0.01
Site II					
VEG	0.05	0.06	0.05	0.05	0.01
VEG	0.06	0.05	0.14	0.08	0.05
NON-VEG	0.06	0.17	0.14	0.12	0.06
NON-VEG	0.05	0.11	0.05	0.07	0.03
TOP	0.05	0.11	< 0.05	0.07	0.03
20-cm DEPTH	0.05	0.06	–	0.06	0.01
Site III-PRIOR					
LAND	0.07	0.07	0.05	0.06	0.01
WATER	< 0.05	0.13	0.07	0.08	0.04
Site III-NEW	< 0.05	< 0.05	< 0.05	< 0.05	–
Site IV					
IN	0.07	0.77	0.08		
OUT	< 0.05	0.07	0.07	0.06	0.01
Site V					
Ship channel	0.07	< 0.05	0.07	0.06	0.01
At dredge	0.18	–	–	0.18	–
Dredge north	0.10	0.13	0.10	0.11	0.02
Dredge south	0.05	0.05	0.09	0.06	0.02

was found dominantly in the organic fraction and Fe in the residuals. They concluded that sequential extraction procedures such as the one developed by Tessier<sup>[17]</sup> give a greater understanding of sediment dispersion and sedimentation patterns.

Hillier et al.<sup>[27]</sup> studied the fractionation of Pb in stream sediments collected near Leadhills/Wanlockhead in southwest Scotland. Lead was also measured using X-ray powder diffraction to determine the mineral phase that Pb is bound and compared with Pb concentrations. They found that the bulk of Pb was located in the carbonate mineral cerussite. This mineral was found associated with the silt fraction of sediments and a

minor component of clay minerals of less than 6  $\mu\text{m}$  size. The presence of Pb attached to fine-grained sediment particles suggests that mobility of Pb in the environment probably occurs through physical movement of fine sediment particles.

Zachariadis et al.<sup>[28]</sup> measured the concentrations of Pb, Cd and Hg in surficial sediments collected from two gulfs in Northern Greece. Sampling was done over a four-year period. Samples were digested using nitric, perchloric, and hydrofluoric acids in high-pressure steel bombs with closed Teflon cups. Results were analyzed statistically accounting for annual, seasonal, and spatial variations. Annual and spatial distributions of heavy metals accounted for variations in concentrations. Soto-Jimenez et al.<sup>[29]</sup> determined the concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in surface sediments in and around oyster beds in Mazatlan Bay (southeast Gulf of California) in an area influenced by sewage outfalls. Enrichments of Cu, Ni, Pb, and Zn found in north to south transects resulted from sewage outfalls. The bioavailable metal concentrations and enrichments in sediments correlated with metals found in the oyster, *Crassostrea irredescens*.

Sivakumar et al.<sup>[30]</sup> measured the trace metals Cr, Cu, Fe, Pb, and Zn in industrial effluents and soils. They used a wet ashing method to digest the samples. Elevated concentration of these metals appeared to alter the physiology of plant species and showed toxic effects on plant leaves, stems, roots, and flowers. Gregory et al.<sup>[31]</sup> determined the concentrations of 12 metals including Cd, Cr, Cu, Fe, Hg, and Zn in sediment from 130 stations near a discharge point into offshore waters. They determined that dispersive x-ray microanalysis could be used to trace the pathway of metals through the water column to the sediment, however, this method lacked the sensitivity necessary for all metals studied. They proposed the use of both FAAS and X-ray methods of analysis be used to produce a rapid, cost-effective procedure. Hamed and El-Moselhy<sup>[32]</sup> collected sediment samples from the Gulf of Suez, Aqaba Gulf, and Red Sea during June 1998. They measured concentrations of Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb, and Zn in these sediment samples with the results showing that the most affected region in the Egyptian Red Sea was the Gulf of Suez, particularly the northern portions of Suez Bay that receives sewage and industrial effluents from Suez City. All other studied areas showed relatively low concentrations.

Hardaway et al.<sup>[33]</sup> used the Toxicity Characteristic Leaching Procedure (TCLP) to measure the concentrations of the metals Cr, Cu, Hg, Pb, and Zn in extracts from the leaching test. The study was done on sediments taken from Bayou d'Inde located in southwestern LA, USA. Bayou d'Inde has been reported severely contaminated by numerous industrial and municipal outfalls along its length and fishing advisories have been issued for this bayou. Sediments were crushed to pass a 20-mesh sieve

(<0.85 mm), well below the recommended 9.5 mm mandated by the TCLP extraction method. Despite the small particle size used, none of the studied metals from heavily contaminated sediments leached in sufficient quantity to exceed the EPA limits as defined by the TCLP method. Table 8 gives typical results of TCLP extractions and reveals that the extraction procedure did not leach heavy metals, suggesting that the metals are mainly in bound states and not readily leached from sediments and thus not readily bioavailable.

Nwajei and Gagophein<sup>[34]</sup> measured the concentrations of Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, and Zn in sediments of Lagos Lagoon, Nigeria. Samples were collected in 1998 and measured concentrations ranged widely between metals and between sampling sites. The ranges in metal concentrations (mg/kg) were Cd 0.13–8.60, Pb 4.1–296, Ni 11.6–149, Cr 23–167, Cu 4.8–103, Zn 27–324, Fe 10,600–85,500, Mn 276–748, Co 6.4–42, Hg 0.04–0.53 mg/kg dry weight. Highest concentrations of metals were obtained

**Table 8.** TCLP Extracts<sup>a</sup> from Sediments Taken from Bayou d'Inde Along with the Primary and Secondary Water Quality Standards and TCLP Limits. Reprinted from Hardaway et al.<sup>[33]</sup> with Permission of the Authors

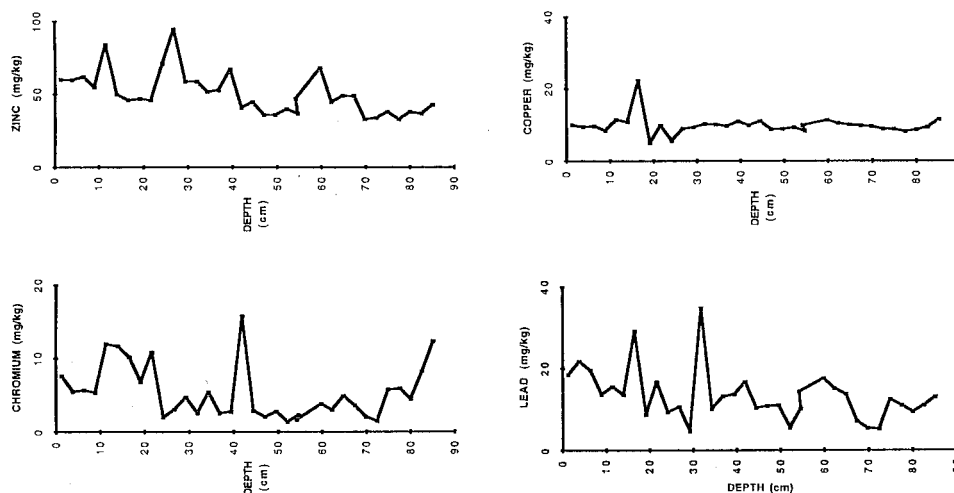
Core	Sample Depth (cm)	Cr (mg/L)	Cu (mg/L)	Hg (mg/L)	Pb (mg/L)	Zn (mg/L)
I	1	0.3	1.2	< 0.001	2.0	18
	29	1.5	1.3	0.035	5.0	4.8
	55	0.5 (2.1)	1.6 (1.6)	0.003 (0.009)	3.0 (5.4)	2.3 (5.1)
II	1	0.5	1.1	< 0.001	1.0	4.6
	29	0.2	0.3	< 0.001	1.0	0.8
III	1	0.2	1.2	0.005	2.0	11
III	24	0.2 (0.3)	1.1 (1.3)	0.002 (0.005)	1.0 (2.0)	11 (12)
	50	0.2	1.2	0.006	2.0	19
	1	0.08 (0.05)	0.3 (0.05)	< 0.001 (0.004)	0.8 (2.0)	0.9 (1.3)
IV	22	0.1	0.3	0.002	0.8	2.7
	MCLs	0.1	1.3	0.002	1.3	5
TCLP (MCL × 100)		10	130	0.2	130	500

<sup>a</sup>Concentration in parentheses are duplicate analysis for the core depth above.

for sediment collected near the village of Iddo. El-Masry and Friedman<sup>[35]</sup> determined the concentrations of Co, Cu, Fe, Ni, Pb, and Zn in 11 bottom sediment samples collected in Lake Mariute, a shallow brackish-water lake adjoining the Mediterranean coast near Alexandria, Egypt. They also used X-ray diffraction techniques to determine percent carbonate and clay minerals in sediment. Carbonate minerals were found to be low-Mg calcites and aragonite, while clay minerals were mainly smectite and illite. Trace element distribution in sediments correlated with carbonate mineralogy, allowing insight into diagenetic history of the sediments. Lake Mariute sediments had metal concentrations exceeding USEPA criteria for polluted lake water and sediments. Locatelli et al.<sup>[36]</sup> measured concentrations of Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in sediments collected in the Marano River ecosystem near Bologna, Italy. They found that sediments have been impacted by local pollution sources.

Oulabi et al.<sup>[37]</sup> reported on the concentrations of Na, K, Ca, Mg, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in sediments collected at run-off points of 17 springs across Lebanon. The purpose was to assess the impact of anthropogenic pollution on the health of these springs. The following ranges in metal concentrations were found in sediments: 0.05–47% Ca, 0–2.5% K, 0.24–4.2% Fe, 0–641 mg/kg Cr, 0–268 mg/kg Zn, 0–96 mg/kg Ni, 0–1356 mg/kg Mn, 6.6–79 mg/kg Pb measured as dry weight. Barook and Labweh springs were found to have high concentrations of trace metals, with a few others having moderately high concentrations. Zereini and Urban<sup>[38]</sup> measured Pt in soils, sediment and street dust to investigate the impact of exhaust gas from catalytic converters. They optimized the Dokimasie method by using pollutant aggregation to lower detection limits to the ppb level, followed by high-pressure disaggregation. The solubility, mobility, and the geochemical properties were described. The main emissions of Pt were found to be the metallic form and Pt was transported by air. Course particles containing Pt are highly localized but fine particles carry Pt great distances by wind.

Aucoin et al.<sup>[39]</sup> measured the trace metals Cr, Cu, Pb, and Zn in fish and sediment cores taken from Lake Boeuf located in southeastern La, USA. Lake Boeuf is an important recreational fishing lake and many species are caught and eaten locally. The presence of large number of chemical plants, refineries, etc., in the local area along the Mississippi River led them to study the lake for possible contamination and to establish baseline concentrations for future water-way uses. Sediment samples were digested using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in microwave digestion vessels. Concentrations of these trace metals in core samples did not vary with depth in cores and had concentrations similar to unpolluted areas in the general vicinity. Figure 4 shows the variation of studied metals with core



**Figure 4.** Variation in the concentration of Cr, Cu, Pb, and Zn in core VI with depth in the core. The depth profiles and metal concentrations in the remaining cores are similar to the variation in core VI. Core VI is thus used to illustrate the variation of metals with depth in Lake Boeuf. Reprinted from Aucoin et al.<sup>[39]</sup> with permission of the authors.

depth. The graphs show a nearly constant concentration with depth and low concentrations. Suspected pollution sources have not impacted this important recreational lake.

Gundacker<sup>[40]</sup> used two bivalve species, (*Anadonta* and *Unio pictorium*); two gastropod species (*Radix Ovato* and *Vivaparvus*) as biomonitors for moderately metal-polluted areas along the Danube River near Vienna Austria. Samples were collected from April 1993 to May 1994 at six sites. Cadmium, Cu, Pb, and Zn was measured in all samples and metal bioaccumulation varied greatly between sampling sites, metal, and mollusks species. Bivalve species studied had concentrations that were related to sediment concentration as expected due to their close association to sediment. Sharma et al.<sup>[41]</sup> studied the association of metal pollution to the functional response of freshwater ecosystems. Trace metals measured included Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. High adsorption of Cd and Zn were found in sediments in association with polluted waters. Bichhdi Pond (near city of Debari) receives Zn smelter waste and naturally contained the highest levels of Cd and Zn. Results of metal determinations on Zooplankton in water bodies along the Berach River system revealed five distinct limnological regions ranging from unpolluted to polluted.

Biodiversity and richness tended to decrease as concentrations of metals in sediments increased.

Alemdaroglu et al.<sup>[42]</sup> studied major and trace element distributions in sediments from four sampling sites located in Lake Egidir, Turkey. They measured the concentrations of Cd, Cu, Fe, Mn, Ni, Pb, and Zn for each station. Concentrations of studied metals fell within the levels expected for unpolluted sediments. However, two stations had statistically higher concentrations suggesting that metal pollution has been added to the study area, particularly the stations with higher concentrations. Wilson and Robinson<sup>[43]</sup> reported on the presence and concentrations of the trace metals Co, Cr, Fe, Mn, Mo, and Ni in sediments in lakes adjacent to a coal-fired power plant near Houston, Texas. Sediments were collected from a depth of 20–30 cm. Higher concentrations of metals were found in the upper part of sediment cores, as expected from diagenesis. The study was considered a measurement of the present day baseline as urbanization and industrial development has continued to increase over the past few years.

Trimble et al.<sup>[44]</sup> measured the concentrations of Cu, Hg, Pb, and Zn in seventy-nine cores taken from 66 sampling sites in sediments of the Steinhatchee River within the Big Bend Management Area along the North Central Florida Gulf of Mexico coastline. The purpose was to establish baseline concentrations of these metals and other physical and chemical parameters. The metals were normalized against reference elements Al and Fe with the stronger correlations found for Al as the normalizing element. The study found little evidence for metal contamination across the study area. Lead and Hg were found to be carried through atmospheric deposition over great distances and thus are not necessarily indicators of activities associated with the estuary. Anomalous concentrations of Cu and Zn do originate from pollution sources in the estuary. Copper did not correlate well with the normalization to Al, further indicating the possibility of contamination.

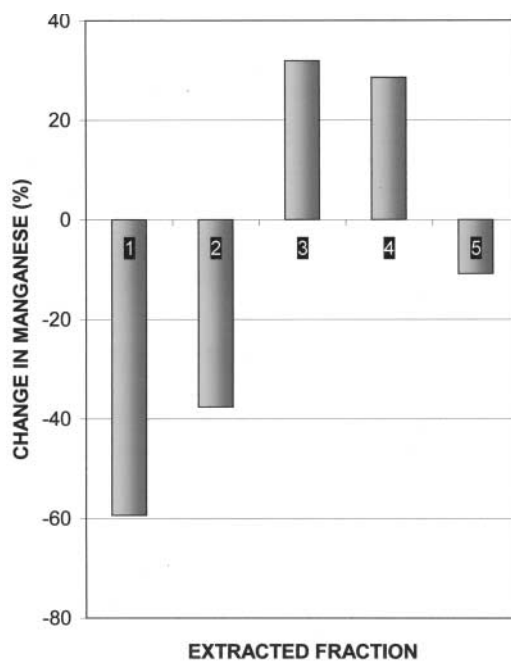
Beck and Sneddon<sup>[45]</sup> recently published a review article detailing the environmental studies that used soils and sediments as the matrix that records changes in metal concentrations used to assess historical impacts. This review focused on environmental studies done in southwestern LA. It gives a summary of common techniques for sampling, typical extraction procedures, summarizes sample collecting gear and corers, and gives a summary of studies done in this important estuary. Gauthreaux et al.<sup>[46]</sup> used a modified sequential extraction procedure<sup>[17]</sup> to speciate the chemical forms of Mn in sediment samples taken from Sabine National Wildlife Refuge, Louisiana. Manganese concentrations were determined for five different fractions for each sample (exchangeable, carbonates, Fe/Mn oxides, organics, and residual). Table 9 compares the concentrations measured in the five

**Table 9.** Results for the Duplicate Analysis of Mn in Soils and Sediments Collected at Sabine National Wildlife Refuge. Reprinted from Gauthreaux et al.<sup>[46]</sup> with Permission of Authors

Sample ID	Manganese by fraction/mgkg <sup>-1</sup>				
	1	2	3	4	5
Site II A	21.6	221	256	35.7	35.1
Site II A dup	16.1	241	222	29.8	Lost
Site II B	14.8	256	206	64.8	50.8
Site II B dup	12.5	282	173	31.5	42.2
Site II C	13.4	173	140	22.4	35.2
Site II C dup	3.2	206	160	29.2	Lost
Site II-VEG B	2.6	105	478	188	31.0
Site II-VEG B dup 1	2.8	108	495	167	25.0
Site II-VEG B dup2	3.4	89	388	150	42
Site IV B	13.6	10.0	10.0	15.0	2.0
Site IV B dup	13.2	10.0	20.0	20.0	2.0
Site V C	18.8	50.0	35.0	105	20.6
Site V C dup	24.0	30.0	50.0	85	3.0

extracted fractions with duplicate analysis. Agreement between sample and sample duplicate results is excellent and demonstrates the reliability and reproducibility of the sequential extraction procedures. These methods may not extract completely the designated fraction because the chemical procedures may alter the distribution of the metals in subsequent fractions, thus fractions are operationally defined. Sediments sampled were dredge spoils taken from ship channel sediments that were placed on top of existing soils that had subsided. The study was designed to describe the impact of these dredge spoils on emerging biota following marsh restoration. Results revealed an Mn pumping model, that suggested that Mn is being concentrated near the sediment surface by environmental conditions. Figure 5 shows the enrichment of Mn in the vegetated areas as compared to the adjacent non-vegetated areas. The shift of Mn to the oxides and organic phases shows the impact of native grass species on the accumulation of Mn into surface sediments. Increased Mn concentration measured at the surface is about 10-fold higher when compared to preexisting soils. Table 10 summarizes the literature used in this review for Section A.





*Figure 5.* Net change in percentage of Mn by fraction comparing Site II-VEG A & B with Site II A-E. The designation Site II-VEG A, B refer to replicate samples collected in areas of heavy vegetation, A-E are samples collected adjacent to the vegetated areas where vegetation had not reemerged. Reprinted from Gauthreaux et al.<sup>[46]</sup> with permission of the authors.

### B. Recent Method Development

Flame atomic absorption spectroscopy has been used for the analysis of many metals in a wide variety of samples, such as soil, sediment, biota, water, etc. It is necessary to get elements to be measured into solution, so a large number of dissolution procedures have been developed and are still being developed. This section focuses on new separation procedures developed over the past three years in a wide variety of matrices.

Elik and Adkay<sup>[47]</sup> studied the effects of ultrasonic excitation on the sequential extraction of Sr from sediments. They compared their results with results using the sequential extraction procedure developed by Tessier.<sup>[17]</sup> The ultrasonic extraction procedure reduced analysis time from 21 to 1.7 h.

Table 10. Applications of Atomic Absorption to Sediment Analysis

Elements	Matrices	Object of Analysis	Digestion Method	Special Procedure	Reference
Cr, Cu, Fe, Mn, Ni, Pb, Zn	Dredge spoils, sediment	Spoils effect on marsh recovery	Tessier seq. extraction		Gauthreaux et al. <sup>[16]</sup>
Cr, Cu, Fe, Pb, Zn	Monitoring	effect of sewage outfalls	Tessier seq. extraction	Core samples	Kwon and Lee <sup>[18]</sup>
As, Cr, Cu, Mn, Ni, Pb, Zn	Monitoring	Pollution	Tessier seq. extraction	Upper 10 cm sediment	Weisz et al. <sup>[19]</sup>
Cr, Cu, Fe, Mn, Ni, Pb, Zn	Dredge spoils, sediment	Spoils effect on marsh recovery	Tessier seq. extraction		Gauthreaux et al. <sup>[20]</sup>
Cr, Cu, Pb, Hg, Zn	Sediment	Monitoring	Digestion bombs	HNO <sub>3</sub> , H <sub>2</sub> O <sub>2</sub>	Hardaway et al. <sup>[21]</sup>
Cu <sup>2+</sup>	Soil	Sorption capacity	Soil + Cu <sup>2+</sup>	Shake sediment in Cu <sup>2+</sup> sol'n	Marosits et al. <sup>[22]</sup>
Cd, Cs, Hg, Mn, Ni, Pb, Zn	Soil-mushrooms	Uptake of metals	Wet ashing	HNO <sub>3</sub>	Rácz and Oldal <sup>[23]</sup>
SiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , Na <sub>2</sub> O, K <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub>	Siliceous material	Effect of SiO <sub>2</sub> on dissolution	Fusion	Oxalic acid-LiCO <sub>3</sub> Litetraborate	Lau et al. <sup>[24]</sup>
Hg	Sediments	Monitoring	Cold vapor		O'Rourke et al. <sup>[25]</sup>
Cu, Fe, Zn	Sediment	Monitoring	Tessier seq. extraction		Kwon et al. <sup>[26]</sup>
Pb	Sediments	Monitoring	Digestion	Fractionation	Hillier et al. <sup>[27]</sup>
Cd, Hg, Pb	Surficial sediment	Monitoring		HNO <sub>3</sub> , HClO <sub>4</sub> , HF	Zachariadis et al. <sup>[28]</sup>
Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Surface sediments	Effect on oyster beds	Wet ashing	HNO <sub>3</sub>	Soto-Jimenez et al. <sup>[29]</sup>
Cr, Cu, Fe, Pb, Zn	Industrial effluents/soils	Toxicity	Wet ashing		Sivakumar et al. <sup>[30]</sup>
Cd, Cr, Cu, Fe, Hg, Zn	Offshore sediments	Metal pathway	Wet ashing		Gregory et al. <sup>[31]</sup>

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Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb, Zn	Offshore sediments	Monitoring	Wet ashing	Hamed and Moselhy <sup>[32]</sup>
Cr, Cu, Hg, Pb, Zn	Sediments	Toxicity	TCPLP	Hardaway et al. <sup>[33]</sup>
Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Zn	Sediments	Monitoring	Wet ashing	Nwajei and Gagophein <sup>[34]</sup>
Co, Cu, Pb, Fe, Ni, Zn	Sediment	Monitoring	Wet ashing	El-Masry and Friedman <sup>[35]</sup>
Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn	Sediments	Monitoring	Wet ashing	Locatelli et al. <sup>[36]</sup>
Na, K, Ca, Mg, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Spring water and sediment	Monitoring	Wet ashing	Oulabi et al. <sup>[37]</sup>
Pt	Soil metals from catalytic converters	Contamination	High-pressure disaggregation	Zereini and Urban <sup>[38]</sup>
Cr, Cu, Pb, Zn	Fish and sediments	Monitoring	Digestion bombs	Aucoin et al. <sup>[39]</sup>
Cd, Cu, Pb, Zn	Bivalves and sediments	Bioaccumulation	Digestion bombs	Gundacker <sup>[40]</sup>
Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Sediments	Ecological response	Wet ashing	Sharma et al. <sup>[41]</sup>
Cd, Cu, Fe, Mn, Ni, Pb, Zn	Sediments	Monitoring	Wet ashing	Alemdaroglu et al. <sup>[42]</sup>
Co, Cr, Fe, Mn, Mo, Ni	Sediments	Response to coal-fired plant	Core samples	Wilson and Robinson <sup>[43]</sup>
Cu, Hg, Pb, Zn	Sediment	Monitoring	Southwest Louisiana	Trimble et al. <sup>[44]</sup>
Metals	Sediment	Review		Beck and Sneddon <sup>[45]</sup>
Mn	Sediment	Migration	Tessier seq. extraction	Gauthreaux et al. <sup>[46]</sup>

Precision was based on analysis of 21 samples and yielded an average relative standard deviation of 9.2, 10.3, 11.7, 8.6, and 12.8% for exchangeable, carbonates, oxides, organic, and residual fractions, respectively. Recoveries of Sr using a reference standard ranged from 75 to 101%. Alves et al.<sup>[48]</sup> developed an experimental procedure for direct sediment analysis for the extraction of Cu, Pb, and Zn. Slurries of sediments were treated by addition of 6 M HNO<sub>3</sub> and 2% (m/v) NH<sub>4</sub>Cl, followed by sonification. Percent recoveries for Cu, Pb, and Zn were 96.4 ± 4.9, 99.7 ± 4.0, and 97.0 ± 4.0, respectively, using a standard reference material.

Zelano et al.<sup>[49]</sup> studied surface organic and inorganic ligand sites using suspensions of sediments containing known masses of sediment samples. The relationship between the concentrations of Cd, Cr, Cu, Fe, Mn, Pb, and Zn and concentrations of ligand sites was determined. Validity of the method was checked by comparing calculated values of ligand bound Cu(II) as a function of pH. Soylak et al.<sup>[50]</sup> also developed a preconcentration/separation method for the determination of Cr(III), Cd(II), Bi(III), and Co(II) using a Diaion Hp-20 resin. Metal ions were fixed on the column as 8-hydroxyquinoline complexes and subsequent desorption with 1 M HNO<sub>3</sub> in acetone. Effects of the presence of alkaline salts, and parameters such as pH, amounts of oxine, type of eluent were studied. Recoveries of > 95% (± 9%) were found using standard reference sediment with a limit of detection between 23–305 ng/g for studied analyte ions.

Alvarez et al.<sup>[51]</sup> have compared leaching properties of two existing leaching procedures for the analysis of Cd, Cr, Pb, and Zn. They compared their leaching results with methods previously developed by Tessier<sup>[17]</sup> and Gupta<sup>[52]</sup>. Samples used in the study were collected from a potentially impacted marine estuary in southern Brazil. They compared the total metal concentration in the extraction techniques against total metals determined from acid digested subsamples. In general, there was good agreement in mass balances between the extraction techniques, but with inconsistencies in the extraction of Cd. The Tessier method mass balances showed acceptable agreement with recoveries ranging from 87–100%. Bottom sediments showed the greater differences in metal concentrations; with significant proportions of metals, with the exception of Cr, being found in easily extractable forms. Merdivan et al.<sup>[53]</sup> studied solid liquid extraction behavior of the transition metal ions (Cu(II), Co(II), Ni(II), Cd(II), and Pb(II)) using *N,N*-dibutyl-*N'*-benzoylthiourea as the extractant. Samples were extracted from paraffin (58–60°) and metal concentrations determined at a temperature of 65.0 ± 0.5°C. Effects of equilibration time, pH of the aqueous phase, concentration of extractant, and solid solvent used were studied to determine optimum extraction conditions. Interferences due to other ions in solution were investigated. This method was then applied to

sediment samples and favorable results for recoveries and reproducibility were found.

Lima et al.<sup>[54]</sup> developed an ultra-sound extraction and compared the results with slurry sampling and microwave-assisted acid digestion for the metals Cd, Cu, and Pb in sediment samples. A two-fold increase in precision and better detection limits were found when compared to over microwave extractions. Extraction conditions optimized included nitric acid concentrations, sonication time, sonication power, sample mass, and particle size for each element analyzed. For Cd, optimum conditions were 0.2–3.0% m/v slurry 0.5% HNO<sub>3</sub>, 2 min sonication at 15 W, for Cu and Pb optimum conditions were 0.2–2.0% m/v slurry 5.0% HNO<sub>3</sub> 5 min at 35 W. Particle size was set at < 30 mm and extraction recoveries found were: Cd 95–105%, Cu 90–101%, and Pb 88–98%. Detection limits for the extraction using 2.5% m/v sediment mix was 15 ng/g.

Nowka et al.<sup>[55]</sup> developed a direct solid sampling GFAAS method for determination of Pb, Cr, and Mn in deposits found on the surface of buildings. Results were compared with similar results measured with conventional FAA determinations after samples were extracted using microwave aqua regia protocols and/or aqua regia–HF digestions. Agreement was satisfactory when extractions were done on standard reference materials. Test samples with masses between 0.029 and 0.756 mg gave an overall precision of about 10% relative standard deviation. Difficulties were found when the method was applied to difficult matrices and these problems are discussed in detail.

Gomez et al.<sup>[56]</sup> developed a sequential extraction procedure to characterize the partitioning of elements in sediments collected in the Odiel Marshes Natural Park, Spain. They found that NH<sub>4</sub>CH<sub>3</sub>CO<sub>2</sub> was superior to MgCl<sub>2</sub> and NaCH<sub>3</sub>CO<sub>2</sub> when introducing samples to the AA, however, exchangeable and carbonate fractions could not be separated. Readsorption of elements was not detected except for extractions of Hg. The second step of the extraction procedure involved repeated extractions with NH<sub>2</sub>OH–HCl and H<sub>2</sub>O<sub>2</sub>–NH<sub>4</sub>CH<sub>3</sub>CO<sub>2</sub> to produce complete extractions of elements bound to oxides and organic matter phases. Elements measured using this extraction procedure were As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. They compared the optimized procedure with a low selectivity sequential extraction procedure and found that the classical methods overestimated As, Cr, and Ni concentrations in the oxide fraction and underestimated the As, Cd, Cr, and Ni in the exchangeable + acid–base fractions.

Tokalioglu et al.<sup>[57]</sup> tested a new sequential extraction procedure for determining speciation of trace metals in sediments. Results obtained from a reference soil sample were compared to the sequential extraction of sediments collected from lakes of a water-laden area of Sultansazligi, Kayseri,

Turkey. Metals extracted using the developed extraction procedure were Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn. Acetic acid, hydroxyl ammonium chloride, hydrogen peroxide plus ammonium acetate, and aqua regia were the extractants used in the four-stage extraction. Recoveries of all metals were quantitative (>95%). Sums of metals extracted from the four extraction steps were compared to total metal in the sample and found to be in excellent agreement. Limits of detection were determined for each of the four extraction steps and found to vary from 0.04 to 0.69 mg/kg.

Batki et al.<sup>[58]</sup> used a three-step sequential extraction procedure to partition the trace metals Cd, Cr, Cu, Pb, and Zn into different chemical fractions. Sediments were collected from the eastern Aegean Sea, Turkey during the period of July and August 1994. Leachants used in this three step extraction procedure were: hydroxylamine hydrochloride–acetic acid, hydrogen peroxide, and nitric–perchloric acids. Metals were dominantly extracted from the nitric–perchloric acid fraction. However, Pb was found in the first fraction of sediments collected from the northern part of the Aegean Sea due to high organic content of this area. Total concentrations of Cd, Cr, Cu, and Zn were highest in Ismar Bay, while Pb was highest in Edremit and Izmir bays. On the other hand, Salvador et al.<sup>[59]</sup> used microwave-assisted pretreatments to dissolve antidandruff shampoos to determine concentrations of Cd, Se, and Zn. The procedure involved the use of HNO<sub>3</sub> to digest shampoo samples placed in a closed cup digestion vessel and irradiated at 800 W for a few minutes. The limit of detection was found to be 0.11 mg/L for Se, and recoveries ranged from 100 to 106%. The limit of detection for analysis of Cd and Zn were 0.09 and 0.078 mg/L, respectively. The method was able to reproduce concentrations of metals given on the labels. It was concluded that the microwave method yields precise and accurate determination of Cd, Se, and Zn in commercial shampoos.

Chakrapani et al.<sup>[60]</sup> developed a simple, rapid, and cost effective method for determination of Ag, Au, and Pd in geological samples. The method is based on the use of a aqua regia–HCl to decompose samples followed by adsorption of metals on powdered charcoal (AC) at a pH ~ 1 in HCl. The analytes were quantitatively adsorbed on charcoal (better than 92%). Accuracy of the method was determined by analyzing five Canadian (CANMET) standard reference materials. No standards were available for Pd, so the accuracy of measurement was determined using standard additions. The method was applied to several geological samples down to 0.1 ppm (10 g samples) within ±10% R.S.D. ( $n=5$ ). Arslan and Tyson<sup>[61]</sup> compared several procedures for determination of Ca, Mg, and Sr in soils based on analysis of two NIST reference materials. Samples were digested in HF and HNO<sub>3</sub> acids in sealed vessels in a microwave oven and in Teflon beakers. Boric acid was added to the digested samples to destroy excess HF

and to prevent the precipitation of  $\text{LaF}_3$ . Potassium was added as an ion suppressor for the FAA analysis. Analysis of Ca required complete removal of silica, but Mg could be determined in the presence of silica. Measurement of Sr required a nitrous oxide–acetylene flame after removal of silica but the concentration of Sr was found to be consistently low as compared to reference standards. Güçlü et al.<sup>[62]</sup> studied the adsorption of free- and bound metal ions (complexes) onto various hydrous oxide type sorbents using EDTA as the model ligand. Metal ion–EDTA mixed solutions containing stoichiometrically amounts or excess amounts of either constituent were used to develop a suitable method for determination of metal complex + free ligand or metal complex + free metal (Cd or Pb). The technique is based on determination of all EDTA (free or bound) species converted to iron complexes after addition of  $\text{Fe}(\text{NO}_3)_3$ , and heating to  $80^\circ\text{C}$  for 1 h, and all metal (free or bound) species were determined using FAAS. All unbound  $\text{Fe}^{3+}$  species were determined by a thiocyanate spectrophotometric method. Concentrations in each phase could then be calculated by differences between separated phases above. This method requires fewer instruments and is, thus, more direct and simple for determining adsorption of Cd and Pb and may be effective in metal adsorption modeling in true environmental simulations.

Quinaia et al.<sup>[63]</sup> conducted a comparative study of  $\text{C}_{18}$  immobilized on silica, activated carbon and a polyurethane foam, as sorbents for Pb complexed with *O,O*-diethyl-dithiophosphate. A simple system consisting of a peristaltic pump, a manual injector–commutator and a mini-column filled with sorbent was used to process the complex in a 1.0 M HCl medium. Ethanol was used as the eluent, and the richest 150  $\mu\text{L}$  fraction was collected and measured by a flame atomic absorption spectrometer. Results indicate that  $\text{C}_{18}$  has superior retention performance in comparison to the other two materials. Tunceli and Türker<sup>[64]</sup> used flame atomic absorption spectrometry to determine Ag after preconcentration on Amberlite XAD-a6 resin from thiocyanate solution. This study investigated the effect of pH, nature of complexing agent, sample volume, flow rate, the type, and concentration of elution solution on preconcentration efficiency. Results indicate that a quantitative recovery of thiocyanate complex of silver was obtained from nitric acid solution (pH 2) to be  $99.20 \pm 0.07\%$ . The maximum preconcentration factor was 75 with a detection limit of Ag of 0.047 mg/L. The maximum adsorption capacity of Ag onto Amberlite XAD-16 was 4.66 mg/g. A relative error of 6.25% was obtained using this procedure to determine the amount of Ag in a standard alloy. Heyden et al.<sup>[65]</sup> studied the use of Kohonen neutral networks to diagnose calibration problems in flame atomic absorption spectrometry. Calibration lines were measured daily in AAS. A method is discussed that will evaluate the quality of those lines that

give a fast diagnosis. These results are then compared to a decision support system that uses classical statistical methods to classify lines. It was determined that both techniques are comparable with both having a predictive error rate  $< 10\%$ .

Quintar et al.<sup>[66]</sup> examined the influence of variable sample volume and constant added standard on the determination of Cr, Cu, and Ni. Results indicated that the two techniques are not equivalent for all cases. Taher<sup>[67]</sup> used atomic absorption spectrometry to determine ultra trace amounts of Zn after preconcentration with ion pairs of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenyl and ammonium tetraphenylborate on microcrystalline naphthalene and also by a column method. Calibration curves were found to linear between 0.05–4.0 ppb in dimethylformamide solution. Determinations of 1.0 ppb of Zn gave a mean absorbance of 0.124 with a relative standard deviation of 1.3%. This technique was used for trace determinations of zinc in various standard samples.

Khalid and Chaudhri<sup>[68]</sup> developed a standardized digestion procedure for the determination of heavy metals in biological materials by flame atomic absorption spectrometry. Copper, Fe, Mn, and Zn were determined in biological samples by dissolution in a mixture of nitric acid and perchloric acid. Results from this procedure were validated against certified values reported by NBS and IAEA standard reference materials and found to be in good agreement.

Jorhem<sup>[69]</sup> examined metal content in foods after dry ashing. A method was developed for the determination of Cd, Cu, Fe, Pb, and Zn in foods by flame atomic absorption spectrometry after dry ashing at  $450^\circ$ . Liver paste, applesauce, minced fish, wheat bran, and milk powder were among the foods studied. Reproducible relative standard deviations for different metals studied are as follows: Pb (20–50% for concentrations of 0.040–0.25 mg/kg), Cd (12–35% for concentrations of 0.001–0.51 mg/kg), Zn (4–8% for concentrations of 0.7–38 mg/kg), Cu (7–45% for concentrations of 0.51–45 mg/kg), and Fe (11–14% for concentrations of 4–216 mg/kg).

Yebra et al.<sup>[70]</sup> examined an on-line continuous precipitation–dissolution flow system for determination of Cd in mussels. The method is a rapid, sensitive, accurate and precise flame atomic absorption method and is based on the continuous precipitation of cadmium as an ion pair between tetraiodocadmiate and quinine, followed by dissolution of precipitate with ethanol. Results obtained were in agreement with certified values for reference materials. Cadmium concentrations were determined in the range of 0.25–5.5  $\mu\text{g/g}$  and the method has a high tolerance to interferences.

Zhou et al.<sup>[71]</sup> developed a microwave digestion procedure for fish tissues (muscle and liver). Many parameters were studied such as the time



and power of the microwave system, composition of digestion solution, and adjustment of oxidation state of Se and Hg prior to analysis. Accuracy of the procedure was determined using certified reference materials. This technique was used on fish tissues obtained from Ramsey Lake (Sudbury, Canada). Results indicate that Cu and Se were more efficiently accumulated in liver whereas Hg was found concentrated in muscle tissue. Fish feeding habits could partially explain differences in tissue concentrations of the three elements. Table 11 summarizes the literature used in this review for Section B.

### C. Metal Preconcentration Methods from Water Samples

This section focuses on new preconcentration methods for elemental analysis of water samples using flame atomic absorption spectrometry. In most cases, element concentrations are too low for direct analysis, so preconcentration allows the analyst to determine the presence and concentrations of metals in dilute solutions. The main problem is to prevent contaminating samples of interest. Methods are presented for a variety of aqueous solutions.

Zih-Perényi et al.<sup>[72]</sup> developed an on-line preconcentration system to concentrate the metals Co, Ni, Pb, and V prior to analysis. The system utilizes a miniature column packed with iminodiacetic acid ethyl cellulose located in line, with solution pulled through the system using a peristaltic pump. Airflow passed through the column to evacuate it between sampling loading, washing, and elution. Samples were eluted directly to the AA using nitric acid. The system was used to determine concentrations of V, Co, and Pb in mineral waters and Ni in seawater. Detection limits in  $\mu\text{g/L}$  were determined to be 0.058 (Co), 0.022 (Pb), 0.067 (V), and 0.062 (Ni) with relative standard deviations R.S.D. ( $n=5$ ) of  $<5\%$  at 0.4–1.0  $\mu\text{g/L}$  concentrations. Narin et al.<sup>[73]</sup> also developed a preconcentration method for determination of Cd, Co, Cr, Cu, Mn, Ni, and Pb in natural water samples. This technique involves sorption of metals on columns packed with pyrocatechol violet complexes on charcoal. Optimum pH for adsorption of metal ions was 4–8. Metals were then eluted from the column with 1 M  $\text{HNO}_3$  in acetone. Analysis of the metals Cd, Co, Cr, Cu, Mn, Ni, and Pb were found to be reproducible as determined using this method in water samples. Relative standard deviations (R.S.D.) varied from 3 to 8% ( $n=10$ ) with detection limits less than 70 ng/L reported. Ellis and Roberts<sup>[74]</sup> utilized a flow injection system to separate Cd, Cu, Mn, and Pb from saline solutions to minimize problems of analyzing metal concentrations in saline solutions. A micro-column packed with Chelex 100 resin was used for all separations.

**Table II.** Applications of Atomic Absorption to Development of New Methods of Analysis

Elements	Matrices	Object of Analysis	Digestion Method	Special Procedure	Reference
Sr	Sediments	Sr extraction	Sequential extraction	Ultrasonic excitation	Elik and Adkay, <sup>[47]</sup>
Cu, Pb, Zn	Sediment	Metal extraction	Direct sediment analysis	Treated slurries	Alves et al. <sup>[48]</sup>
Cd, Cr, Cu, Fe, Mn, Pb, Zn	Sediments	Study ligand sites	Ion exchange	Resin and 8-hydroxy-quinoline	Zelano et al. <sup>[49]</sup>
Cd, Cr, Pb, Zn	Sediments	Compare extraction methods	Sequential extraction methods		Alvarez et al. <sup>[51]</sup>
Cr <sup>3+</sup> , Cd <sup>2+</sup> , Bi <sup>3+</sup> , Co <sup>2+</sup>	Water	Metal ion extraction	Preconcentrate/separation	Resin and 8-hydroxy-quinoline	Soylak et al. <sup>[50]</sup>
Cu <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup>	Water	Metal ion extraction	Solid/liquid extraction	<i>N,N</i> -dibutyl <i>N</i> '-benzoylthiourea on paraffin	Merdivan et al. <sup>[53]</sup>
Cd, Cu, Pb	Sediments	Compare slurry and microwave methods	Ultra-sound extraction		Lima et al. <sup>[54]</sup>
Cr, Mn, Pb	Deposits on walls	Direct solid sampling	Microwave extraction	Aqua regia	Nowka et al. <sup>[55]</sup>
As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	Sediments	Sequential extraction			Gomez et al. <sup>[56]</sup>
Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	Sediments	Sequential extraction			Tokalioglu et al. <sup>[57]</sup>

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Cd, Cr, Cu, Pb, Zn	Sediments	Sequential extraction	Batki et al. <sup>[58]</sup>
Cd, Se, Zn Au, Ag, Pd	Shampoo Geological samples SRM	Microwave extraction Aqua regia-HCl HF-HNO <sub>3</sub> digestion	Salvador et al. <sup>[59]</sup> Chakrapani et al. <sup>[60]</sup> Arslan and Tyson <sup>[61]</sup>
Ca, Mg, Sr	Hydrous oxide sorbants Water	EDTA complexes	Güçlü et al. <sup>[62]</sup>
Cd, Pb	Water	<i>O,O</i> -diethyl-dithiophosphate complexes Concentrate Ag	Quinária et al. <sup>[63]</sup>
Pb	Water	Kohonen neural networks Effect of volume and constant added volume Preconcentration of Zn	Tunçeli and Türker <sup>[64]</sup> Heyden et al. <sup>[65]</sup> Quintar et al. <sup>[66]</sup>
Ag	Water	Digestion method	Taher <sup>[67]</sup>
Cr, Cu, Ni	Water	Dry ashing	Khalid and Chaudhri <sup>[68]</sup> Jorhem et al. <sup>[69]</sup>
Zn	Water	Precipitation-dissolution flow system Microwave digestion	Yerba et al. <sup>[70]</sup>
Cu, Fe, Mn, Zn	Biological materials Foods Mussels	Method parameters	Zhou et al. <sup>[71]</sup>

Separations were optimized by detailed studies of the effects of ammonium acetate buffer concentration, pH, and concentration of buffer flush on separations. Recoveries were found to range from 99.8 to 100% for assayed samples collected in the Severn Estuary.

Ohta et al.<sup>[75]</sup> used yeast to preconcentrate Cu in river water. The bed used in the separation of Cu was 3.5 mg/mL of 2-ammonium hydrogen phosphate, with an optimal cultivation time and temperature of 2 h and 40°C, respectively. Method detection limits were found to be 85 pg/mL in river waters. Recoveries of Cu were found to range from 93–100%. Matrix interferences were removed after the cultivation step and no chemical treatments were required. Ferreira et al.<sup>[76]</sup> developed a preconcentration method for Cu in water samples using Amberlite XAD-2 resin loaded with calmagite reagent to adsorb Cu. Concentration of Cu can be determined in the range of 0.0125–25.0 µg in 25–250 mL samples, respectively. Detection and determination limits were found to be 0.15 and 0.50 µg/L, respectively. Selective tests showed that the following metals and concentrations did not interfere with the Cu determination: Ca<sup>2+</sup> (500 mg/L), Mg<sup>2+</sup> (500 mg/L), Sr<sup>2+</sup> (50 mg/L), Fe<sup>3+</sup> (10 mg/L), Ni<sup>2+</sup> (10 mg/L), Co<sup>2+</sup> (10 mg/L), Cd<sup>2+</sup> (10 mg/L), and Pb<sup>2+</sup> (10 mg/L). Precision of the method using seven replicates was found to be 2.42% for Cu masses of one microgram. Carasek<sup>[77]</sup> reported on a simple, fast extraction in xylene of Au for submicrogram concentrations in water samples. Ammonium diethyldithiophosphate (DDTP) was used as the complexing agent. Extractions were carried out until the aqueous to organic phase achieved a 1000-fold preconcentration of metal. Effect of Fe interference was studied and optimized for determination of Au. Average recoveries of 95% were found and a detection limit of 2.9 ng/L determined in deionized water. Carasek et al.<sup>[78]</sup> developed a method to provide highly reliable determinations of Cd and Pb in natural waters. The method provides a preconcentration step involving the extraction of Cd and Pb into 3.5 mL of the complexing agent, dithizone in xylene. Dithizonate complexes were then back-extracted into 0.6 mL of nitric acid. The method was optimized using spiked deionized water. Three sigma detection limits were measured as 0.39 ng/L for Pb and 8.2 ng/L for Cd for microextraction times of 4 min and back extraction times of 1 min.

Adriá-Cerezo et al.<sup>[79]</sup> presented a method for preconcentration and speciation of Cr by the formation of an anionic compound with ethylenediaminetetraacetic acid. Chromium (III) and (VI) are retained on a strong anionic phase followed by elution with 0.5 M saline solution. Retention and elution conditions were optimized and interferences caused by several metal ions and anions were carefully studied. Stated detection limits for the method were given as 0.4 µg/L for Cr<sup>3+</sup> and 1.1 µg/L for Cr<sup>6+</sup>, with a reproducibility of 9%. Speciation results were in good agreement with

values obtained from a standard reference material. Marqués et al.<sup>[80]</sup> developed a new procedure for the speciation of Cr by sequential injection analysis using aluminum microcolumns. The Cr<sup>3+</sup> was retained on the column as anionic complexes and Cr<sup>6+</sup> as a cationic complex. The Cr<sup>3+</sup> was eluted off the column with 2 mol/L NH<sub>4</sub>OH followed by the elution of Cr<sup>6+</sup> with 2 mol/L HNO<sub>3</sub>. The limits of detection for the ions were Cr<sup>3+</sup>, 42 µg/L and Cr<sup>6+</sup>, 81 µg/L. Bağ et al.<sup>[81]</sup> also developed a method for the speciation for Cr in water samples using a sequential injection system. This system separates the Cr ion species by adsorption on *Saccharomyces cerevisiae* immobilized on sepiolite. Optimization was obtained by detailed studies of effects of pH, bed height, flow rate, and sample volume of separation efficiency. The overall recovery of Cr was found to be 96.3 ± 0.2%. Breakthrough capacity for Cr (III) was found to be 228 µmol/L and the method was considered to be highly successful in determining concentrations of Cr (III) and Cr (VI) in spiked and natural river water samples.

Bravo-Sánchez et al.<sup>[82]</sup> reported on a preconcentration method for determinations of Hg and Pb in highly saline water (sea water). Columns tested were 7-4-(ethyl-1-methyloctyl)-8-hydroquinoline (Kelex 100) adsorbed on Bondapak C-18 (Kelex-100/C18), 8-hydroxyquinoline immobilized on vinyl polymer Toyopearl gel (TSK), and also the commercially available resin-Chelex-100. Mercury and Pb were preconcentrated on the minicolumn packed with each of the column packing materials and eluted directly to the AA. Acetic acid buffer (0.5 mL) was used to elute the metals from the column. Each column and metal elution was optimized by detailed studies of effects of column size, pH, other metal ion interferences, eluent, and eluent volume. They found that TSK columns gave better and more consistent results. Column size for the two metals varied, for Pb (1 cm in length and 2.5 mm i.d.) while Hg required a larger microcolumn (5.5 cm in length and 5.0 mm i.d). Analyses were applied to several Asturian coastal aqueous samples that gave consistent results for recoveries of the two metal ions of interest. Burguera et al.<sup>[83]</sup> used a flow injection on-line precipitation–dissolution technique for determination of ultra trace amounts of Be in water samples. Beryllium was precipitated using NH<sub>4</sub>OH + NH<sub>4</sub>Cl solutions and collected in a knotted tube of Tygon allowing other metal ions to flow through the system. The precipitate was washed, redissolved in HNO<sub>3</sub>, a subsample collected, and 6 µg of Lu metered into the subsample. The method was optimized by studying the effect of various metal ions on the recovery of Be. Only Al<sup>3+</sup>, Cr<sup>3+</sup>, and Fe<sup>3+</sup> ions resulted in production of precipitates having large particle sizes. Method detection limits was found to be 25 ng/l with an overall precision of 4.8 and 4.0% ( $n=5$ ) for solutions containing 20 and 200 pg of Be, respectively. Enrichment factors from 7.0 to 10.3 and from 10.5 to 13.8 were determined for precipitation times of

25–38 s and 43–50 s for waste and tap waters. The method was also tested using standard reference materials and spiked samples with satisfactory results reported.

Kékedy-Nagy and Cordos<sup>[84]</sup> measured concentrations of Rb in mineral and well waters using a methane–air flame in an attempt to improve sensitivity. Effects of flame and instrumental parameters such as flame composition, flame height for metal determination, spectral band pass of the monochromator on the emission of Rb in the methane–air flame was extensively studied and optimal conditions found. The best results were found using the 780.0 nm Rb line at an observation height of 11 nm with methane to air ratio of 1.12. Effect of the presence of Ca, Mg, Na, and K was also studied to determine possible interferences. Detection limit of the method was found to be  $2.3 \pm 0.9 \mu\text{g/L}$  obtained in the presence of 200 mg/L of Cs. This method allows direct measurement of Rb in water samples using both external calibration curves and standard addition methods. The method was applied successfully to determination of Rb in natural water samples. Table 12 summarizes the literature used in this review for Section C.

#### D. Metal Studies in Biota

Flame atomic absorption spectroscopy has been used for the analysis of many elements in biotic samples. Applications encompassed quantitative elemental measurements in a wide range of samples such as fish, shellfish, mollusks, mussel, algae, lichens, plant species and clams. Samples are typically extracted and analyzed from many parts of biotic species such as the gills, liver, skin, and muscle.

Avenant-Oldewage and Marx<sup>[85]</sup> measured the bioaccumulation of Cr, Cu, and Fe in the fish *Clarias gariepinus* from two sites on the Olifants River in the Kruger National Park. Gills, liver, muscle, and skin of samples were examined for metal bioaccumulation. Data obtained showed that highest concentrations of Cr were detected in gills, suggesting that they are the prime site of absorption and loss of Cr to and from the aquatic environment. It was inferred that liver serves as a storage and detoxification organ for metals because the liver contained the highest concentrations of Cu and Fe. Dorowolski and Skowronska<sup>[86]</sup> examined muscular tissue of fishes (roach, perch, bream) from the Zemborzyce Reservoir for Cd, Cr, Hg, Pb, and Zn. Results indicate that accumulation of Cd was similar for all fishes examined, while roaches had the highest level of Cr and perches had the highest accumulation ability for Hg, Pb, and Zn. Mollusks were also examined and showed excellent accumulation ability for all studied elements.

**Table 12.** Applications of Atomic Absorption to Water Analysis

Element	Matrix	Object of Analysis	Digestion Method	Special Procedure	Reference
Co, Ni, Pb, V	Natural and sea water	Preconcentrate	Miniature column	Peristaltic pump	Zih-Perényi et al. <sup>[72]</sup>
Cd, Co, Cr, Cu, Mn, Ni, Pb	Natural water	Preconcentrate	Columns	Pyrocatechol complex on Charcoal	Narin et al. <sup>[73]</sup>
Cd, Cu, Mn, Pb	Saline solutions	Preconcentrate	Microcolumn	Chelex 100 resin	Ellis and Roberts <sup>[74]</sup>
Cu	River water	Preconcentrate	Adsorption	2-ammonium hydrogen phosphate	Ohta et al. <sup>[75]</sup>
Cu	Water	Preconcentrate	Amberlite XAD-2	Calmagite reagent	Ferreira et al. <sup>[76]</sup>
Au	Deionized water	Extraction	Ammonium diethyldithiophosphate		Carasek <sup>[77]</sup>
Cd, Pb	Natural waters	Preconcentrate	Dithizone in xylene		Carasek et al. <sup>[78]</sup>
Cr <sup>3+</sup> , Cr <sup>6+</sup>	Water	Preconcentrate/ speciated ions	Formation of anionic compounds	EDTA	Adriá-Cerezo et al. <sup>[79]</sup>
Cr <sup>3+</sup> , Cr <sup>6+</sup>	Water	Speciation	Aluminum microcolumns		Marqués et al. <sup>[80]</sup>
Cr ions	Spiked and river water	Speciation	Sequential injection	Sepiolite	Baq et al. <sup>[81]</sup>
Hg, Pb	Sea water	Preconcentrate	Columns	Kelex-100 on Bondapak C-18	Bravo-Sánchez et al. <sup>[82]</sup>
Be	SRM's and spiked water	Precipitation/ dissolution	Precipitated with NH <sub>4</sub> OH + NH <sub>4</sub> Cl	HNO <sub>3</sub>	Burguera et al. <sup>[83]</sup>

Perez Cid et al.<sup>[87]</sup> studied variations of Cd, Cu, Ni, Pb, and Zn concentrations in fishes (*Anguilla anguilla*, *Mullus surmuletus*, *Trigla lucerna*, *Mugil cephalus*, *Chelon labrosus*, *Liza aurata*, *Dicentrarchus labrax*) in the Rio de Aveiro (Portugal). Metal concentrations for all fishes examined were very low in fish muscle. Concentration levels of Cd, Ni, and Pb were less than 0.15 mg/g while Cu levels were typically between 0.5 and 1.1 mg/g (wet wt.). The most abundant element found in all the fishes was Zn with values between 4.7 and 12 mg/g. *A. anguilla* species tended to have higher concentrations of Ni (0.16–0.40 mg/g) and Zn (20 mg/g). Results obtained for elements studied were well below the recommended levels by specific legislation for these aquatic organisms. Slightly different results were obtained by Mitra et al.<sup>[88]</sup> when they found that Pb (examined Cu, Pb, Zn) was the most abundant element in muscles of six edible coastal fishes. Results also showed that accumulation of heavy metals was species specific. Ansari et al.<sup>[89]</sup> studied the edible muscle tissues of five fish species *Rohu* (*Labeo rohita*), *Calbans* (*Labeo calhasu*), *Mori* (*Chirrhina inrigala*), *Ichagga* (*Rita rita*), *Singliaree* (*Osteobagrus*) marketed in Multan. Results showed that muscle tissue contained higher amounts of K, Ca, Na, and Mg, moderate quantities of Zn and Fe and lesser amounts of Cu and Mn. Cadmium and Pb levels were below detection limits.

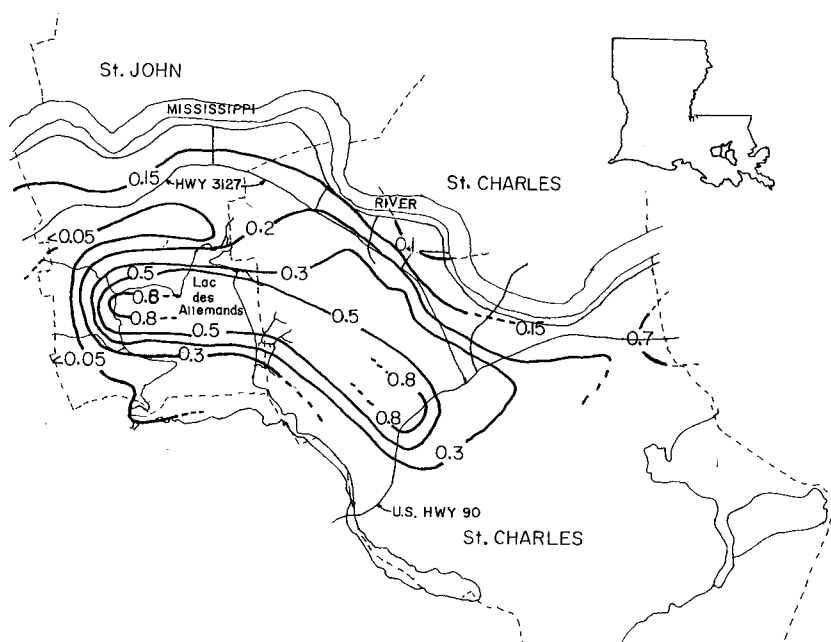
Sho et al.<sup>[90]</sup> examined trace element contents (As, Cd, Cu, Mn, Pb, and Zn) in fishes/shellfishes on the Korean markets and evaluated their safety. Samples were digested with acids. Fish samples contained the following trace element concentrations (mean, mg/kg); Pb: 0.29, Cd: 0.020, As: 0.84, Cu: 0.66, Mn: 0.57, Zn: 6.03. Shellfish samples contained the following trace element concentrations (mean, mg/kg); Pb: 0.38, Cd: 0.51, As: 1.08, Cu: 3.84, Mn: 3.25, Zn: 25.24. It was concluded that trace element contents in fishes and shellfishes on the market were similar to those reported by other investigators, and that average weekly intakes of Pb and Cd were approximately 10% of tolerable weekly intake.

Locatelli and Torsi<sup>[91]</sup> developed an analytical procedure and sample mineralization for analysis of Hg in food matrixes such as mussel, clams, and fishes. Sample digestion used a concentrated supra-pure H<sub>2</sub>SO<sub>4</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> mixture. Mercury levels were determined by cold vapor atomic absorption spectrometry. Christopher et al.<sup>[92]</sup> and Mitchell et al.<sup>[93]</sup> used cold vapor atomic absorption spectroscopy for the analysis of Hg. Mitchell et al.<sup>[93]</sup> examined lichens across St. Charles, St. James, and St. John Parishes, Louisiana. The lichens *Ramalina stenospora* and *Parmotrema prae-sorediosum* were collected from limbs of live oak trees in a three-parish area of southeast Louisiana. Concentrations of metals measured in the two lichen species are compared in Table 13. No statistically significant differences in metal were found between the two lichen species. Highest concentrations



**Table 13.** Concentration of Hg in Two Lichen Species (*R. stensopora* and *P. praesorediosum*) for Sampling Sites where Both Species was Found. Reprinted from Mitchell et al.<sup>[93]</sup> with Permission of the Authors

Sampling Site	Ramalina	Parmotrema	Mean
3127-A	0.33	0.22	0.28
3127-C	0.26	0.34	0.30
3127-D	0.23	0.22	0.23
3127-G	0.14	0.24	0.19
90-A	0.25	0.26	0.26
90-B	0.24	0.22	0.23
90-C	0.83	0.68	0.76
90-D	0.75	0.58	0.67
90-F	0.40	0.32	0.36
90-G	0.21	0.24	0.23
90-H	0.22	0.20	0.21



**Figure 6.** Distribution of Hg concentration (mg/kg) in *Ramalina stensopora* and *Parmotrema praesorediosum* in the study area. Reprinted from Mitchell et al.<sup>[93]</sup> with permission of the authors.

**Table 14.** Comparison of Measured Concentrations of Hg in Sample and Sample Duplicate. Reprinted from Mitchell et al.<sup>[93]</sup> by Permission of the Authors

Sampling Site	Mercury Concentration (ppm)	
	Sample	Sample Dup
3127-5	0.08	0.10
3127-7	0.29	0.30
3127-10	0.24	0.17
3127-11	< 0.05	< 0.05
3127-C	0.26	0.31
3127-G	0.21	0.15
90-A	0.25	0.28
90-F	0.40	0.38

detected were above 0.8 ppm and fell off rapidly with increasing distance from possible sources of trace metals. Results of the analysis plotted in Figure 6 show concentration contours trending from the southeast to northwest. It was concluded that the spatial distribution of mercury concentrations correlated with predominant wind patterns for the region. Table 14 gives a comparison of Hg concentration in lichen samples with results of analysis of a subsample (duplicate), and agreement is excellent.

Sures et al.<sup>[94]</sup> determined Cd and Pb concentrations in the archiacanthocephalan *Macracanthorhynchus hirudinaceus*. These results were compared to those results found in the porcine definitive host from a slaughterhouse in La Paz, Bolivia. Results showed that *M. hirudinaceus* contained 85, 85, 56, and 24 times higher lead levels compared with host's muscle, liver, kidney, and intestine, respectively. Cadmium levels were found to be 32 times higher than that of liver and 5 times higher than porcine kidney. Conclusions indicate that the hypothesis that parasites excrete toxic metals with the shells of their eggs is not valid for *M. hirudinaceus* and that arachiacanthocephalans from mammalian hosts are able to bioaccumulate metals.

Jordao et al.<sup>[95]</sup> examined heavy metals inputs to river systems near smelters in Brazil. Concern for chronic poisoning to human populations from smelting of ores was the thrust of this study. Drinking/river water, fish, and plant samples were collected up- and down-river from smelters and analyzed for metals. Background values were collected from spring water (Vicosa and Belmiro Brago) and a dam (Conselheiro Lafaiete) in the area. Results obtained for river water samples were as follows: Fe ( $1323 \pm 45$  mg/L), Mn ( $251 \pm 30$  mg/L), and Cr ( $70.6 \pm 2.5$  mg/L). No significant contam-

ination was found in drinking water samples. Higher than normal concentrations of Cr ( $12.6 \pm 3.7$  mg/L) and Ni ( $7.9 \pm 3.9$  mg/L) were found in plants. Concentrations of Cr were found to exceed the recommended safe levels for human intake in fish samples by a factor of 90.

Szkoda et al.<sup>[96]</sup> studied trace elements in carp tissues (muscles and liver) during the period of 1995–97 for 311 carps collected at fish farms in selected regions of Poland. Results indicated no significant accumulation of As, Cd, Hg, or Pb in samples collected and samples were not dangerous to human health.

Maiti and Banerjee<sup>[97]</sup> studied accumulation of heavy elements in different tissues (muscle, kidney, ovary, liver, gills, and fins) of the fish *Oreochromis niloticus* exposed to waste water. Accumulation of Pb and Cd concentrations were equal in all organs studied. Chromium showed no significant accumulations in any fish tissue. Copper accumulated most in liver and ovaries of fish tissues while Zn tended to accumulate more in ovaries and fins. Results indicate that regular consumption of such exposed fish may lead to increased risk of acute element toxicity in man.

Daoud et al.<sup>[98]</sup> did a residual analysis of some heavy metals in water and *O. niloticus* fish from polluted areas. Samples were collected from three industrial sites in Egypt (Helwan El-Marazek Brige, Kaha, Kafr El-Zayat) during the summer 1998. Water samples were collected near and at various distances from outfalls of local industries. Fish samples were also collected from these same water-sampling sites. Heavy metal concentrations of Cd, Cu, Hg, Pb, and Zn were determined for these samples. Other studies included examining the effect of heat treatment (frying and roasting) on Hg residue in fish tissue. Highest concentrations of Cu, Hg, Pb, and Zn were obtained in water samples from Kafr El-Zayat. The Kaha area contained the highest concentrations of Cd. Helwan fish samples contained the highest concentrations of most heavy metals while Hg tended to be in the Kafr El-Zayat area. Results showed that frying fish had a stronger effect than roasting in decreasing residual Hg in fish samples.

Voegborlo et al.<sup>[99]</sup> studied the Cd, Hg, and Pb content of canned tuna fish. Mercury levels were examined by cold vapor atomic absorption spectrophotometry while Cd and Pb used FAAS. Results found were as follows: Hg (0.20–0.66, average 0.29 mg/g), Cd (0.09–0.32, average 0.18 mg/g), Pb (0.18–0.40, average 0.28 mg/g). Results indicate that tuna fish from the Mediterranean coast of Libya have concentrations well below toxic limits for these metals.

Aucoin et al.<sup>[100]</sup> studied trace metals (Cr, Cu, Pb, Zn) in fish and sediments from Lake Boeuf, southeastern Louisiana. Metals were extracted from fish and sediments using microwave digestion techniques and quanti-

fied by flame atomic absorption spectroscopy. Results did not show any variation in metal concentrations due to species or weight of fish. Seasonal conditions did effect metal concentrations. Ranges in metal concentrations were as follows: Cr (2–15 mg/g), Cu (0.2–4 mg/g), Pb (0.5–9 mg/g), and Zn (10–20 mg/g). Sediment samples studied did not indicate any variation with depth in the core samples (Figure 4). This result suggests pollutant metals have not been inputted to the lake.

Schuerack et al.<sup>[101]</sup> examined the potential use of South African river crab, *Potamonautes warreni*, as a bioindicator species for heavy metal contamination. Samples of adult *P. warreni* were collected from the Mooi River at Noordbrug. Crabs were exposed to 0.2 or 2.0 mg Cd<sup>2+</sup>/L in situ to determine tolerance, uptake and bioaccumulation of Cd. Gills, hemolymph, and digestive gland of crab samples were examined for Cd concentrations. Naturally exposed *P. warreni* showed concentrations of Cd of  $0.74 \pm 0.27$ ,  $0.007 \pm 0.007$ , and  $0.12 \pm 0.09$  mg/g for the gills, hemolymph, and digestive gland, respectively. Samples exposed to Cd had concentrations of  $9.99 \pm 5.09$ ,  $0.012 \pm 0.006$ , and  $0.38 \pm 0.20$  mg/g, respectively. Results indicate that *P. warreni* have transport, storage, and regulatory mechanisms that may be used as a bioindicator species for pollution. Soto et al.<sup>[102]</sup> studied the adsorption of metals (Cd, Cu, Ni, Pb, Zn) by algae. They proposed the use of these organisms as a means to recover metals coming from industrial wastewaters and for purification of contaminated waters. The study focused on the binding capacity of metals in solution by *Chlorella vulgaris*.

A biodiversity study was done by Sharma et al.<sup>[41]</sup> on functional responses of natural systems of freshwater ecosystems to heavy metal pollution. The study focused on the adsorption of Cd and Zn in sediments and the use of zooplankton as bioindicators of stress. Heavily polluted bodies of water were found to be biological deserts that supported only marginal grasses and insects. Gundacker<sup>[40]</sup> used two bivalve species, *Anadonta* and *Unio pictorium* and two gastropods, *Radix ovata* and *Viviparus* as biomonitors to assess impacts of the metals Cd, Cu, Pb, and Zn in moderately polluted waters. Metal bioaccumulation was found to vary strongly with sampling site, metal, and bivalve species. Copper was found to be 20-fold higher in gastropods than bivalves, perhaps indicating a higher Cu regulation capacity in gastropods. Bivalves were found to accumulate other metals, that are correlated to fine sediments, as would be expected from its trophic level.

Zachariadis et al.<sup>[28]</sup> determined the concentrations of Cd, Hg, and Pb in sediments and mussels (*Mytilus galloprovincialis*) to test their ability to record metal variations in a coastal environment. The study was conducted over the previous 4-years and variations of metal concentration with time is

Table 15. Applications of Atomic Absorption to Analysis of Elements in Biota

Element	Matrix	Object of Analysis	Digestion Method	Special Procedure	Reference
Cr, Cu, Fe	<i>Clarias gariepinus</i>	Bioaccumulation	Wet ashing		Avenant-Oldewage and Marx <sup>[85]</sup>
Cd, Cr, Hg, Pb, Zn	Fish-roach, perch, bream	Bioaccumulation	Wet ashing		Doropwolski and Skowronska <sup>[86]</sup>
Cd, Cu, Ni, Pb, Zn	Several fishes	Bioaccumulation	Microwave extraction		Anguilla Perez Cid et al. <sup>[87]</sup>
Cu, Pb, Zn	Several fishes	Bioaccumulation	Wet ashing		Mitra et al. <sup>[88]</sup>
Ca, Cu, Fe, K, Mg, Mn, Na, Zn	Several fishes	Bioaccumulation	Wet ashing		Ansari et al. <sup>[89]</sup>
As, Cd, Cu, Mn, Pb, Zn	Several fishes/shellfish	Bioaccumulation	Wet ashing	Market samples	Sho et al. <sup>[90]</sup>
Hg	Fishes, clams, mussels	Method development	Cold vapor		Locatelli and Torsi <sup>[91]</sup>
Hg	Lichens	Bioaccumulation	Cold vapor		Mitchell et al. <sup>[92]</sup>
Hg	Fishes	Bioaccumulation	Cold vapor		Christopher et al. <sup>[93]</sup>
Cd, Pb	<i>Macrecauthor-hynchus hirudinaceus</i>	Body burdens	Wet ashing		Sures et al. <sup>[94]</sup>
Cr, Fe, Mn, Ni	Plants, fish	Body burdens	Wet ashing		Jordao et al. <sup>[95]</sup>
As, Cd, Hg, Pb	Carp	Body burdens	Wet ashing		Szkoda et al. <sup>[96]</sup>
Cd, Cr, Cu, Pb	<i>Oreochromis niloticus</i>	Up-take of metals	Wet ashing		Maiti and Banerjee <sup>[97]</sup>
Cd, Cu, Hg, Pb, Zn	<i>Oreochromis niloticus</i>	Body burdens	Wet ashing	Effect of cooking	Daoud et al. <sup>[98]</sup>

(continued)

Table 15. Continued

Element	Matrix	Object of Analysis	Digestion Method	Special Procedure	Reference
Cd, Hg, Pb Cr, Cu, Pb, Zn	Canned tuna Fish	Concentration Body burdens	Wet ashing Microwave digestion		Voegborlo et al. <sup>[99]</sup> Aucoin et al. <sup>[100]</sup>
Cd Cd, Cu, Ni, Pb, Zn	<i>Potamonautes warreni</i> <i>Chlorella vulgaris</i>	Bioindicator Bioindicator	Wet ashing Wet ashing		Schuwrack et al. <sup>[101]</sup> Soto et al. <sup>[102]</sup>
Cd, Zn Cd, Cu, Pb, Zn	Zooplankton Two bivalves, two mollusks	Biodiversity Bioindicators	Wet ashing Wet ashing		Sharma et al. <sup>[41]</sup> Gundacker <sup>[40]</sup>
Cd, Pb Cu, Mn, Pb	<i>Mytilus galloprovincialis</i> <i>Perinereis gualpensis</i> <i>Jeldes</i>	Concentration Biomonitor	Wet ashing Wet ashing		Zachariadis et al. <sup>[28]</sup> Bertran et al. <sup>[103]</sup>
Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn Cr, Cu, Pb, Zn	<i>Crassostrea irredescens</i> Various plant species	Body burden Effect on plants	Wet ashing Wet ashing		Soto-Jimenez et al. <sup>[29]</sup> Sivakumar et al. <sup>[30]</sup>

discussed. Bertran et al.<sup>[103]</sup> used *Perinereis gualpensis Jeldes*, a common polychaete, as a biomonitor of heavy metal pollution. They measured the concentrations of Cu, Mn, and Pb in the polychaete. A weak correlation was found between concentration of metals in the polychaete and those found in water and sediments. Soto-Jimenez et al.<sup>[29]</sup> determined the concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the soft tissue of the bivalve *Crassostrea irredescens*. Studied oysters accumulated more Zn, Cu, Ni, Fe, and Cd and less Mn, Cr, and Pb than were available from sediments. Enrichments of these metals and bioavailable metal fractions in the sediments are discussed. The possibility of using this oyster as a biomonitor is also discussed. Sivakumar et al.<sup>[30]</sup> studied various plant species and their effect on metal concentration using conventional wet ashing procedures. Trace elements measured in this study were Cr, Cu, Pb, and Zn. They observed that these trace metals appeared to alter the physiology of some plant species in the study area. These effects were manifested in alterations in the leaf, stem, root, etc. structure and toxic effects. Table 15 summarizes the literature used in this review for Section D.

#### ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of Nicholls State University and the Nicholls Research Council in the production of this manuscript.

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