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Pollution Chronology of Lake Valencia, Venezuela

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Analyses of dated sediments as a means to obtain chronological information on the pollution of aquatic environments has widely been applied (e.g. Charles and Hites, 1986; Jaffé and Hites, 1985; Jaffé et al. 1993; Bloom and Crecelius, 1987; Battiston et al., 1989). The technique is particularly useful for the historical pollution assessment of environments where no prior water quality or environmental pollution data exists. This is often the case in the developing world, where pollution related studies have only started in recent years. In such cases, pollution chronology obtained form dated sediment cores can provide valuable information on pollution trends, baseline information and environmental impact information in general.

Lake Valencia, located in the North-Central Venezuelan Aragua Valley, at an altitude of about 400 m above sea level, is the second largest Lake in the country, and an important source of freshwater in the area. The lake has a surface area of 356 Km^2, a mean depth of 19 m, a maximum depth of 40 m and its drainage basin covers approximately 3,000 Km^2 (Jaffé, 1988). Lake Valencia is a monomictic lake, and is classified as hypereutrophic (Jaffé et al., 1993 and references therein). Large amounts of untreated sewage enters the lake through a variety of small streams, several of which cross major urban/industrial areas such as the cities of Valencia and Maracay. Wastes from the extensive pig-farming activity in the direct proximity of the lake are also discharged directly into Lake Valencia. Due to the elevated nutrient levels in the lake, primary productivity (particularly blue green algae) is extensive, and anoxic conditions in the water column are common during a great part of the year. During wind induced water turnover (October-December) massive fish kills have been reported (Infante et al., 1979).

Even though chronological studies of lake sediments have shown that Lake Valencia has been eutrophic at least for the last two centuries (Jaffé et al. 1993), evolution to a hypereutrophic status in recent decades clearly indicates a degradation of water quality in this environment due to anthropogenic activities. In fact, the Aragua Valley has been one of the areas in Venezuela with the fastest population growth and industrial development, activities which started about 40-50 years ago. As will be shown below, pollution chronology of dated sediments correlates well with the population/industrial developments of the area.

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MATERIALS AND METHODS

Sediment cores were taken in 1989 and 1990 at the deepest part of the central portion of the lake, at a depth of approximately 40 m. A Wildco model 2400 gravity core sampler was used for this purpose. Cores were retrieved and immediately sliced into individual segments of 2 cm thickness and stored in appropriate pre-cleaned sample containers (glass for organic analyses and polyethylene for metals and nutrients). Cores for organic analyses were taken with a metal tube, whilst for the metals a plastic insert was used to avoid sample contamination. Samples for organic analyses were kept frozen until analysis.

Heavy metals such as Cu, Pb, Ni, Zn and Fe were analyzed by atomic absorption spectrometry (AAS). With the exception of Fe, which was analyzed by flame AAS (FAAS) using an air-acetylene flame, heavy metals were determined by graphite furnace AAS (GFAAS) using a Perkin Elmer model 2380 Atomic Absorption Spectrophotometer. Analytical condition were those indicated in the instrument manual with some minor modifications. Quantitative analysis was based on calibration curves prepared with commercially available standards (Merck). Blanks were run throughout the procedure and no significant contamination was observed.

Analyses of aliphatic and aromatic hydrocarbons were performed as well. Sediment samples were first extracted with pesticide grade isopropanol followed by methylene chloride, in as Soxhlet extractor, both for 24 hrs. The extracts were combined, passed over an activated copper column, and fractionated into aliphatic and aromatic hydrocarbons by adsorption chromatography on silica gel (Peltzer et al. 1984). The aliphatic hydrocarbon fractions were spiked with an internal standard (nC_{22} alkene) and analyzed on a Hewlett Packard 5890 Series II capillary gas chromatograph, equipped with a 25 m, 0.2 mm i.d. high performance cross linked methyl silicone gum column, a split-splitless injector and a flame ionization detector (FID). Helium was used as carrier gas, and the oven programmed from 40 to 280 ^{o}C at 6 ^{o}C/min; injector and detector temperatures were both set at 280 ^{o}C.

Aromatic hydrocarbons were analyzed by fluorescence spectroscopy on a dual beam spectrofluorometer from Shimadzu, model RF 520. Excitation and fluorescence emission wavelengths were 310 and 360 nm respectively. Quantitation was done using a calibration curve for an authentic chrysene standard.

Chlorinated hydrocarbons such as pesticides and polychlorinated biphenyls (PCBs) were analyzed by high resolution gas chromatography using a Hewlatt Packard 5890 Series II instrument, equipped with an electron capture detector (GC-ECD, Ni^{63}). Concentrations were determined in the splitless mode as previously described by Sericano et al. (1990). Capillary columns, 30 meters long x 0.25 mm i.d. with 0.25 µm DB-5 film thickness, were temperature-programmed from 100 to 140 ^{o}C at 5 ^{o}C/min, from 140 to 250 ^{o}C at 1.5^{o}C/min and from 250 to 300^{o}C at 10^{o}C/min with 1 min hold time at the beginning of the program and before each program rate change. A hold time of 5 min was used at the final temperature. Injector and detector temperatures were set at 275 and 325^{o}C, respectively. Helium was used as carrier gas. Argon/methane (95:5) was used as the make-up gas. The instrument was calibrated using authentic standards at four different known concentrations to compensate for non-linear response of the electron capture detector.

Phosphates as orthophosphate, were determined using the standard spectrophotometric method by Stricland and Pearsons (1968) adapted for sediments. Briefly, slurries of sediment samples in distilled water were treated with potassium persulfate and sulfuric acid, autoclaved for 1 hr., and filtered through filter paper (Whatman 42). Solutions obtained were treated with the molibdate/ascorbic acid/tartrate reagent and analyzed on a Shimadzu model 150-2 spectrophotometer. Quantitation was achieved by calibration curve methods using potassium orthophosphate as calibration standard.

All reagents and solvents used were of high quality and materials and glassware were properly cleaned prior to analysis. Blanks were performed for all analyses, and in all cases, no significant contamination was observed. Sediment dating was achieved *via* ^{137}Cs dating as described elsewhere (Jaffé et al., 1993).

RESULTS AND DISCUSSION

Depth profiles of the concentrations of metals, aliphatic hydrocarbons, total aromatic hydrocarbons, halogenated hydrocarbons and phosphates were determined for Lake Valencia sediments. Concentration profiles of the metals Pb, Cu, Ni and Cd are shown in figure 1a and b. It can be observed that the metal concentrations increased in recent times. The pronounced concentration increase observed for Pb and Cu shows a strong increment staring in the early 1950s. Ni and Cd also show an increase in concentration at that time, but the shape of the curve is different from that of Pb and Cu. While the depth profiles of Pb and Cu level off after the late 1960s, Ni and Cd continue to increase. The initial increase of the latter in the early 1950s is, however, less pronounced that that of Pb and Cu. This difference may indicate a different source (industrial) for these metals, and a different rate of introduction into Lake Valencia. In any case, the historical profile correlates well with the population/ industrial/agricultural development of the Aragua Valley.

It is interesting to observe, that approximately in 1978, all metal profiles show a temporary decrease in the metal concentrations. This is the case for both the Pb-Cu and Ni-Cd pairs. Similar concentration changes have been reported in the literature (e.g. Crecelius and Piper, 1973). Possible explanations were suggested, such as a reduction in the sedimentation rate due to reduced water discharges during exceptionally dry seasons, and by sediment dilution (by new sediments) due to river diversions. In fact, both factors could have influenced the metal distribution in Lake Valencia sediments. The lake has had a geological history of periodically drying out (Lewis and Weibezahn, 1981) and in 1978 reached its minimum water level in recent history (Medina, 1986). To overcome this problem, the Cabriales River was diverted into the lake *via* Caño Central (in the city of Valencia) in 1979 (Olivo, 1985). It is likely that a combination of both these factors caused the observed concentration decrease of the metals in the sediment core.

Commonly, enrichment factors (EFs) are used to determine the degree of anthropogenic inputs of metals to the environment (Förstner and Wittmann, 1983). EF values for the case of Lake Valencia are indicated in figure 1c and d. These values were calculated based on pre-industrial age metal concentrations normalized *vs.* Fe, as shown by the equation:

$$EF\,(M_x) = \{[M_x]/[Fe_x]\}/\{[M_y]/[Fe_y]\}$$

Where [M] = metal concentration in sediment, x = depth of sediment segment and y = sediment segment at 21-29 cm depth (pre-industrial).

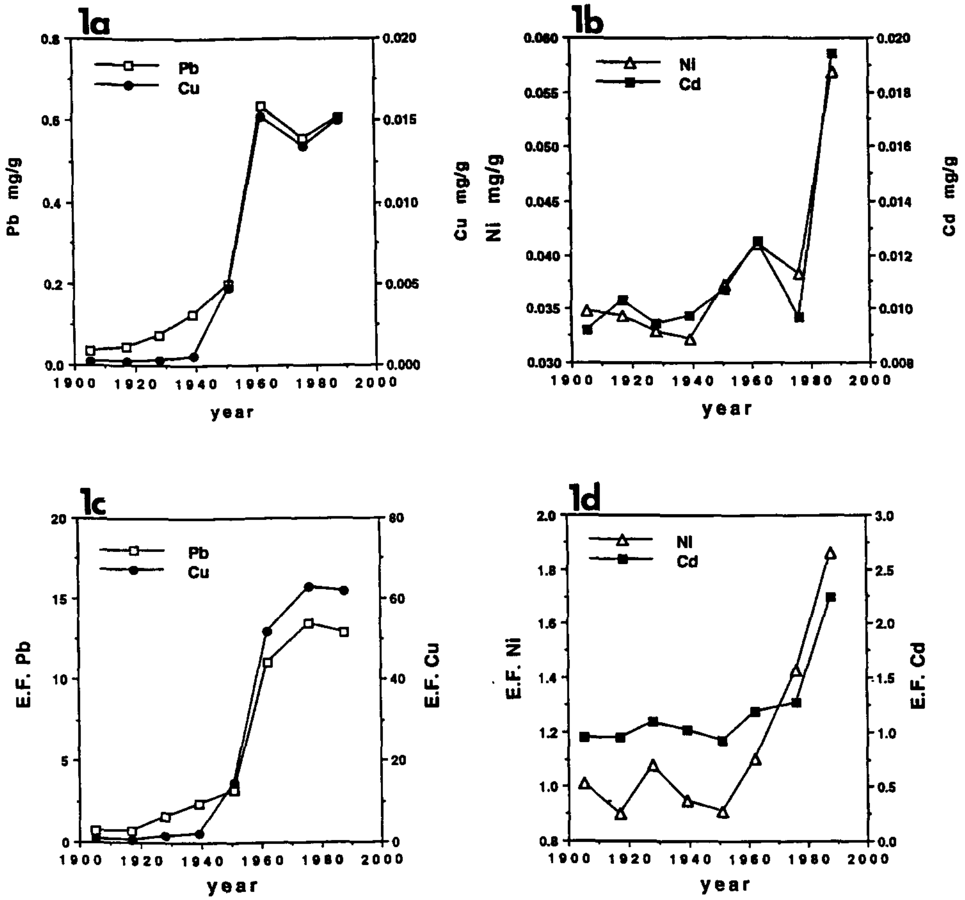

Figure 1: Depth profiles of heavy metal concentrations and enrichment factors (EF) in a dated sediment core from Lake Valencia.

When EFs are used for the metals in Lake Valencia (see figure 1c and d) the concentration drop in 1978-1979, as expected, is not observed, and the profiles are more indicative of the 'real' pollution history of metals to the lake. The values themselves indicate significant metal enrichment in Lake Valencia sediments.

The chronology of phosphorous (as orthophosphate), is shown in figure 2a. As for the metals discussed above, an increment in the phosphorus concentration in recent years was observed, and is likely to be caused by increased municipal (sewers), industrial and agricultural discharges. Orthophosphate levels found were relatively high, ranging from about 50 to 95 mg/g. Previously, several authors had reported on the elevated phosphorus levels (in the order of 100 µg/l) in the lake (Jaffé, 1988; Lewis and Weibezahn, 1983), and suggested this to be the primary reason for the hypereutrophic status of the Lake (Jaffé et al. 1993).

The aliphatic hydrocarbon fraction was composed primarily of n-alkanes, n-alkenes, tri- and pentacyclic triterpenoids and a complex mixture of cyclic and branched hydrocarbons (UCM). The n-alkanes ranged from a carbon number of 15 to 33, with a slight odd over even predominance. This predominance increased with increasing depth

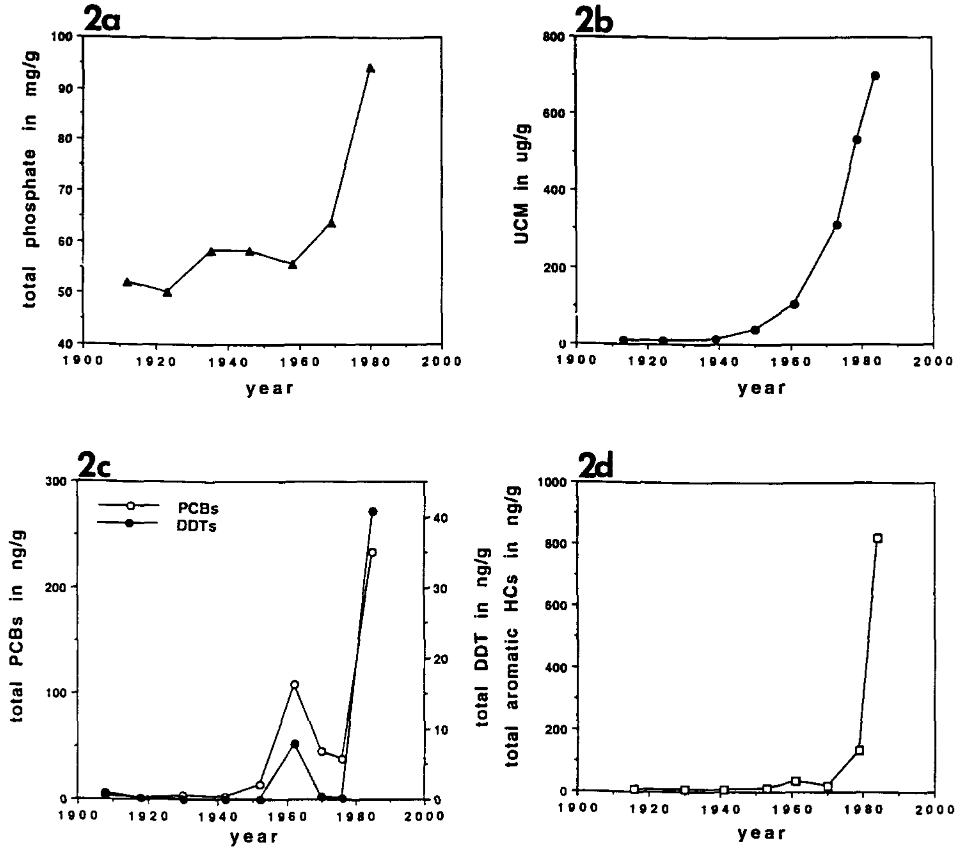

Figure 2. Depth profiles of (a) phosphate, (b) UCM, (c) PCBs and DDTs, (d) aromatic hydrocarbons, in a dated sediment core from Lake Valencia.

in the core. The low carbon preference index (CPI) in the surface sediments in combination with the presence of an UCM is a clear indication of hydrocarbons of anthropogenic origin (e.g. Wakeham and Farrington, 1980). The increment in the UCM concentration with increasing year of deposition (decreasing depth; see figure 2b) has been observed in other lakes (e.g. Wakeham and Farrington, 1980) and has been correlated with the development of anthropogenic activities in the lake's drainage basin. Hydrocarbon mixtures with low CPI and presence of an UCM have fossil fuel sources and are therefore of anthropogenic origin. The triterpenoids found in the samples were of biogenic origin and will be discussed elsewhere. The increment in concentration of UCM in the late 1940s to early 1950s agrees with the general development of Aragua Valley.

Aromatic hydrocarbons were detected in the form of DDE, DDT and PCBs by chromatography and as total aromatics by fluorescence spectroscopy. Only traces of DDT were detected. Graphs of total PCBs, DDTs and aromatic hydrocarbons *vs.* year of deposition, shown in figure 2c and d, indicate that these compounds also increase in abundance in recent years. Surprisingly, however, the trend is different to that of the UCM, which shows an earlier increment than the aromatics. The halogenated components seem to agree to a certain extent with the total aromatics with respect to the very pronounced increment in recent years (1970's; see figure 2c and d). They do, however, show an initial increment at about 1950 followed by a decrease in the late 1960's early 1970's, in a somewhat similar way to the metals. While neither the total aromatics nor the halogenated hydrocarbon distributions are easy to explain, both indicate a significant increment in the anthropogenic activities in the Lake's drainage basin during recent years. Their 'delay' in their increment with respect to the aliphatic hydrocarbons (UCM) may be source related.

In summary, Lake Valencia's pollution chronology clearly correlates with the development of anthropogenic activities in the Aragua Valley. Both domestic as well as industrial and agricultural sources of anthropogenic inputs into the lake, *via* surface runoff, riverine input and atmospheric deposition, are the likely cause of the observed profiles. Increasing population growth, industrial development and agricultural activities, will further contribute to the pollution of the lake. Since evaporation is the sole output of water from the lake, continued introduction of contaminants will further aggravate the already existing problem. It is hoped that environmental control measures, recently implemented by the government, will have a significant effect on the water quality of Lake Valencia in the future.

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