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Arsenic in tree rings at a highly contaminated site

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Abstract

Arsenic concentrations were measured in annual rings, pith, bark, and leaves of five tree species (four genera) from a site highly contaminated with As in Vineland, New Jersey, and two nearby uncontaminated areas. The highest As concentrations were found in bark (0.68±0.89 mg/kg, $n=16$) and leaves (1.9±1.8 mg/kg, $n=4$) from the contaminated area. Tree-ring As levels from the contaminated area (0.28±0.15 mg/kg, $n=32$) were low but still considerably higher than those from the control areas (0.06±0.06 mg/kg, $n=30$). There is a generally positive relationship between soil and tree-ring As levels. The overall low uptake of As by trees contrasts with that of P, a chemical analog for As(V) in aerated soils. Much higher P concentration in sapwood than in heartwood indicates that P is exported into more recently formed wood during the conversion from sapwood to heartwood; this again is drastically different than the behavior of As which is present in sapwood and heartwood at comparable levels. Variable sapwood As concentrations observed in detailed radial profiles of tree-ring chemistry of a pine and an oak from the contaminated site suggest that As is most likely transported among multiple rings within the sapwood. Therefore, tree species for which sapwood is thin (e.g., oak as in this study) should be preferred for reconstructing the history of contamination of a site. Due to the possibility of lateral translocation between growth rings, further studies are necessary to understand within-tree As transport and storage before dendrochemistry can be confidently accepted for such applications.

Keywords: Arsenic; Tree ring; Radial profile; Dendrochemistry

1. Introduction

The behavior and fate of As in the environment have received increasing attention in recent years because of growing evidence of the serious threat to human health posed by this metalloid. For this reason, reconstructing the history of exposure to As at sites that have been contaminated by anthropogenic sources would be very valuable. Dated river and lake sediment cores have widely been used as archives of past inputs of contaminants (Forstner and Wittmann, 1983; Schuck, 1995; Rice et al., 2002). But this approach is not suitable for contaminated soils where datable depth profiles are generally not available or where there is considerable spatial heterogeneity. Furthermore, even laminated sediment records of As contamination are susceptible

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to post-depositional distribution that is unrelated to the input history (e.g., Linge and Oldham, 2002; Martin and Pedersen, 2002; Keimowitz et al., 2005).

Dendrochemistry, the analysis of chemical composition of annual growth rings of trees, has long been used as a method to explore the chronology of exposure to toxic elements in soil or air (e.g., Hagemeyer, 1993). The approach remains controversial, as shown by the comparable number of failed and successful attempts (see reviews by: Hagemeyer, 1993; Watmough, 1997). Several more recent published studies have successfully correlated tree-ring records to historical contamination or mobilization of metals in the soil (e.g., Baes and McLaughlin, 1984; Hagemeyer, 1993; Yanosky and Vroblesky, 1995; Nabais et al., 1996; Smith and Shortle, 1996; Punshon et al., 2003; Devall et al., 2006).

The first study of As compared orchard trees treated with arsenical pesticides and those from adjacent untreated areas, showing some effect of soil As level on tree-ring As content (Martin et al., 2000). The concentrations of As in the bark and pith samples from the treated site were also clearly shown to be elevated relative to the inner xylem rings. On the basis of only 4 xylem ring samples, Martin et al. (2000) concluded that dendroanalysis for As in fruit trees would not yield a reliable chronology of arsenic exposure. We reconsider here the possibility of using As content of tree rings as a marker of past contamination by presenting data for a series of live trees from the highly contaminated Vineland Chemical Superfund site in New Jersey.

Arsenical pesticides were produced by Vineland Chemical for over 4 decades (1950–1994). Before 1977 the company stored by-product arsenic salts in open piles and chicken coops, which resulted in extensive contamination of soils, groundwater, the nearby Maurice River, and Union Lake further downstream (http://www.epa.gov/region02/superfund/npl/0200209c.pdf, accessed April 2006). Recent investigations indicate that As contamination was mostly in the inorganic form, but with a significant contribution from monomethyl-arsenic (MMA) and dimethyl-arsenic salts (DMA). A small wastewater treatment system was installed on the site in 1982, but it was not until 1999 that a massive groundwater pump-and-treat operation was initiated. An excavation and cleanup of an estimated 268,000 tons of soil contaminated with As started in 2003 when tree samples were collected.

For this study, the As content of tree tissues in two oak species (post oak, *Quercus stellata* and white oak, *Quercus alba*), pitch pine (*Pinus rigida*), eastern redcedar (*Juniperus virginiana*), and pignut hickory (*Carya glabra*) growing in soil containing 8–500 mg/kg As was measured (Table 1). The specific oak species was not determined when tree cores were obtained from the field. The results are compared with oak and pine growing in two nearby uncontaminated control areas containing only 1–5 mg/kg As in the soil. Because phosphate is a chemical analog to arsenate, the dominant form of inorganic As in aerated environment, P content in wood and soil samples were also examined and compared to As. Because processes governing the distribution of nutrient element P in trees are relatively well understood (e.g., Meerts, 2002), this comparison could therefore provide insights into the mechanisms of As uptake and transport. The high sensitivity of high-resolution inductively coupled plasma mass spectrometry (HR ICP-MS) used in this study was essential for measuring the As content of

Table 1
Arsenic and phosphorus concentrations in soil samples collected at contaminated and control sites in Vineland, New Jersey

Location #	Depth (cm)	Soil As (mg/kg)	Soil P (mg/kg)
Contaminated area			
4	0–10	52.0	588
	10–20	38.1	191
	20–30	20.7	107
	Mean	*36.9*	*295*
7	0–10	387	1536
	10–20	662	448
	20–30	449	264
	Mean	*499*	*746*
9	0–10	30.7	459
	10–20	27.6	211
	20–30	23.1	162
	Mean	*27.1*	*277*
13	0–10	3.8	129
	10–20	21.0	209
	20–30	4.1	31
	Mean	*9.6*	*123*
14	0–30	7.9	106
15	0–30	35.2	615
16	0–30	15.9	163
17	0–30	23.0	235
18	0–30	9.3	116
Average		***74±160***	***297±230***
Uncontaminated control areas			
19	0–30	2.8	93
22	0–30	4.1	188
24	0–30	4.6	187
25	0–30	1.6	38
26	0–30	3.6	62
27	0–30	3.9	79
28	0–30	5.5	73
29	0–30	2.4	41
30	0–30	2.7	93
Average		***3.5±1.2***	***95±56***

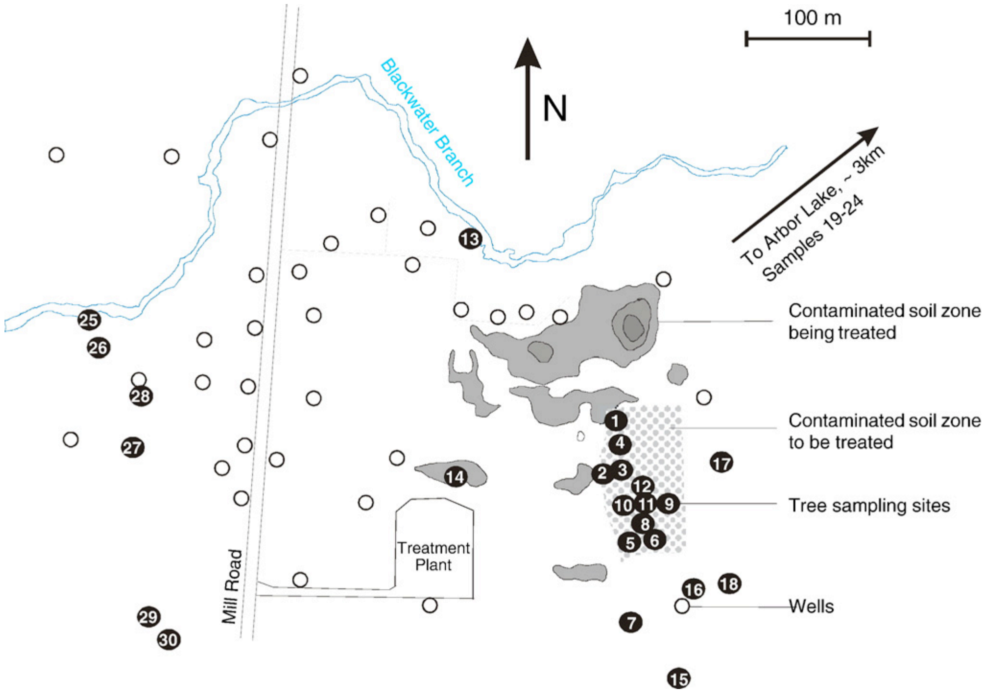

Fig. 1. Sketch map of the Vineland Superfund Site showing the extent of soil contamination and sampling locations.

single tree rings and allows simultaneous measurement of P concentrations.

2. Methods

A total of 17 live trees (numbered 1–18, see Table 2) were sampled at the Superfund site, and 13 additional live trees were sampled in two uncontaminated control areas (Fig. 1). Trees 7, 13, 15–18 from the Superfund site were located outside contaminated soil zones outlined for treatment by site mitigation personnel, whereas the remaining trees were located within these zones (Fig. 1). Trees numbered 19–24 were sampled near Arbor Lake, about 3 km upstream of the contaminated site. Trees 25–30 were collected only about 100 m from the western boundary of the Superfund site, on the other side of Mill Road (Fig. 1). The two latter groups of samples include two genera (pine and oak) found at the contaminated site and are considered controls. During coring, many trees on the site were found to be rotten inside despite looking healthy from outside. The rotten cores were not analyzed for this study. A 0.5-kg soil sample was collected with a spade to a depth of 30 cm within the root zone of most trees that were sampled. At each of the four locations within the contaminated site, a total of 3 soil samples were collected at different depths (Table 1).

Tree samples were collected using a Haglof increment corer at breast height (~ 1.4 m above ground). The corer removes a 5.15 mm dowel of stem tissue along the radial axis of a tree. The cores were placed in clear plastic straws in the field, sealed, and taken to the Tree-Ring Laboratory at Lamont-Doherty Earth Observatory for analysis. The cores were air dried for 1–3 days, mounted in wooden core mounts with water-based glue, and polished with progressively finer sandpaper up to 600-grit in order to expose the ring boundaries for identification (Stokes and Smiley, 1968; Fritts, 1976). Because few tree-ring width data are available for this specific area, the ring widths of trees from the control site were used to establish a cross-dated ring width chronology, following standard dendrochronology methods (Stokes and Smiley, 1968; Fritts, 1976; Cook and Kairiukstis, 1990). This absolutely-dated time series of annual ring width was used for comparison with the growth patterns of trees from the contaminated areas. The accuracy of the time series of cross-dated tree-ring width was evaluated using the quality-control program COFECHA (Holmes, 1983).

Individual rings or, depending on sample size, groups of rings spanning up to 3 years, were analyzed in their entirety for two cores from the contaminated area. The cores were dissected with a stainless-steel surgical scalpel, taking care to remove all glue residues. The first core was collected from a pine tree (#13), on the bank of a small stream along the northern margin of the generally contaminated area (Fig. 1). The core was selected to address the possibility of As remobilization from the contaminated stream sediments during a major flood in 1985. The second core (#14) was obtained from an oak tree that had been cut down from a highly contaminated soil area only a few weeks before sampling (Fig. 1). The bark from this tree was also divided into five sub-samples for chemical analysis from the vascular cambium to the outer bark surface. For all other trees, only the bark, outer-most ring(s), inner-most ring(s), and the pith were analyzed. For all except eight trees pith was missed during coring. The outer-most ring(s) and inner-most ring(s) were analyzed to represent sapwood and heartwood samples, respectively. In addition to woody tissue samples, leaves were collected from four different trees (of different species) within the contaminated area, each in triplicate from the same branch. The leaf and bark samples were rinsed briefly with purified water (>18 MΩ) in an ultrasonic bath to wash off dust particles that might contain high levels of As.

The soil, wood and leaf samples were dried separately in an oven for 24 h at approximately 60 °C. Soil samples (~0.05 g) were digested in a mixture of HNO_3, HF, and $HClO_4$, following a procedure developed for digesting marine sediments (Zheng et al., 2003). Wood and leaf samples (0.02–0.15 g dry weight) were placed in acid-cleaned 7-ml Teflon vessels, followed by the addition of 1.0 ml of high purity HNO_3 (Optima, Fisher). The vessels were tightly capped and digested overnight at ~150 °C. Upon complete dissolution, ~0.5 ml of high purity 30% H_2O_2 (J.T. Baker) was added to each sample and the combined solution was slowly evaporated at ~70–80 °C to decompose the remaining organic fragments. The HNO_3–H_2O_2 digestion procedure was repeated if any black residue was still visible. After digestion and complete evaporation, 0.5 ml of 10% HNO_3 was added to the warm vessel. The solution was transferred to 0.5-ml tubes and centrifuged at 3000 rpm for 10 min to separate any minor insoluble residue. A 0.2 ml aliquot of the supernatant was diluted with 1.8 ml of an internal calibration solution containing 250 µg/l Ge.

Arsenic and P concentrations in the digest solutions were measured on a magnetic sector HR ICP-MS (Cheng et al., 2004). The use of Ge as an internal calibration element corrects for the reduction in nebulization flow that is often observed for organic digests. Arsenic data were acquired at high mass resolution (~10 K) to eliminate possible polyatomic interference from ArCl. Standard reference materials, either marine sediment (SRM-2702) or tomato leaf (SRM-1573a, National Institute of Standards Technology), were analyzed with each batch of samples. The average of two SRM-2702 measurements was 44.9±0.8 mg/kg, which is indistinguishable from the reference value of 45.3±1.8 mg/kg. A total of 9 measurements of SRM-1573a gave an average As value of 110±15 (±13%) µg/kg, which is also consistent with the reference value of 112±4 µg/kg. Three blanks were included with each batch of analyses. The average

Table 2
Arsenic and phosphorus concentrations in bark, outer-most ring(s), and inner-most ring(s) of four wood species at Vineland, New Jersey

Core #	Species	# of rings (±5)	As concentrations (mg/kg)			P concentrations (mg/kg)	
			Bark	Outer ring	Inner ring	Outer ring	Inner ring
Contaminated area							
01	Oak	70	0.22	–	0.40	–	101
02	Oak	79	0.13	0.25	0.27	256	42
03	Oak	70	–	0.18	–	–	–
10	Oak	85	0.22	0.46	0.99	187	45
14	Oak	83	2.34	0.22	0.53	361	22
16	Oak	99	0.40	0.10	0.41	307	–
17	Oak	91	0.21	0.10	0.08	391	24
18	Oak	98	0.18	0.10	0.21	230	29
07	Pine	32	0.17	0.54	0.36	220	29
08	Pine	37	0.41	0.13	0.18	170	51
13	Pine	86	1.10	0.37	0.20	756	37
04	Cedar	55	2.75	0.22	0.27	100	57
06	Cedar	35	0.16	0.12	0.36	161	38
09	Cedar	58	0.33	0.20	0.40	292	34
15	Cedar	60	0.12	0.28	0.08	248	39
05	Hickory	60	2.07	0.17	0.30	71	38
12	Hickory	82	0.14	0.20	0.14	96	57
	Average		**0.68±0.89**	**0.23±0.13**	**0.32±0.22**	**256±167**	**43±19**
Uncontaminated control areas							
19	Oak	101	0.03	0.03	0.03	283	16
20	Oak	104	0.04	0.03	0.05	440	172
21	Oak	105	0.04	0.04	0.05	355	28
22	Oak	102	0.03	0.05	0.07	474	35
23	Oak	105	0.02	0.08	0.06	273	76
24	Oak	97	0.02	0.09	0.06	488	12
30	Oak	57	0.02	0.04	0.04	352	97
31	Oak	50	0.09	*0.34*	0.03	273	72
25	Pine	83	0.07	0.02	0.02	280	46
26	Pine	62	–	0.04	0.01	121	53
27	Pine	88	0.04	0.12	0.07	234	116
28	Pine	89	0.06	0.09	0.02	229	36
29	Pine	92	0.06	0.12	0.08	205	96
	Average		**0.04±0.02**	**0.06±0.04**	**0.05±0.02**	**308±109**	**66±46**

Table 3
Arsenic concentrations in pith and leaf samples of Vineland trees

	Tree species	Pith[a]	Leaf[b]
Contaminated area	Cedar	–	3.14±0.48
	Pine	0.52 (n=3)	3.64±1.33
	Oak	1.62 (n=2)	0.29±0.08
	Hickory	0.30 (n=2)	0.45±0.11
Control areas	Oak	0.09 (n=1)	–

All units are mg/kg.

[a] The mean concentration from cores that contained pith tissue.

[b] The confidence interval = 1-standard deviation of the mean for leaf concentration.

procedural blank was 0.5±0.3 ng (n=9) for tree-ring analyses. The effective detection limit of ~0.01 mg/kg for As in tree rings (assuming a ~0.1 g sample) was estimated as three times the standard deviation of the blank measurements.

3. Results

3.1. Total As and P in soil

Although one of the control areas was only 100-m away from the site across the Mill Road and located downstream near the Black Water Branch (Fig. 1), the soil As levels at this location are low (1–5 mg/kg) and similar to the other control area about 3-km away (Table 1). Six trees (7, 13, 15, 16, 17, and 18) from the site were located outside the zone outlined by mitigation personnel for soil remediation, but the soils from these locations were clearly contaminated with As (9–499 mg/kg), even more so than the soil from the zones that were remediated (8–37 mg/kg). Hereon, all trees within the site are therefore grouped and considered to represent contaminated conditions. Although highly variable, concentrations of total As in soil samples from the entire contaminated area are generally much higher than the average background level of 3.5 mg/kg for samples collected from the two control areas. Concentrations of As also vary somewhat with depth in the contaminated area, but not following any obvious pattern (Table 1). Soils from the contaminated area generally contain higher P levels than that of the control areas (3 times more on average), and P concentrations decrease rapidly with depth.

3.2. Arsenic concentrations in tree rings and other tissues

Concentrations of As are very low in most woody tissue samples (Table 2). At the contaminated site, for instance, As concentrations in tree rings range from 0.08–0.99 mg/kg, several orders of magnitude below the As content of surrounding soils (8–499 mg/kg). Concentrations of As are higher in bark and leaves from the contaminated area, but still <4 mg/kg (Tables 2 and 3). A simple calculation indicates that a 1000-kg tree (dry weight) contains ~0.3 g of As, which is equivalent to the amount of As in 30 kg of soil (assuming average As contents for wood and soil are 0.3 mg/kg and 10 mg/kg, respectively).

Trees from the contaminated area are significantly enriched in As compared to trees in the control areas (Table 2, Figs. 2 and 3). Arsenic concentrations in the bark, outer-most ring(s), and inner-most ring(s) of 17 trees from the contaminated area average 0.7±0.9, 0.2±0.1, and 0.3±0.2 mg/kg, respectively. Excluding an oak sapwood sample that contains anomalously high As levels (0.34 mg/kg), the bark, outer-most ring(s), and inner-most ring(s) of 13 trees from the control areas average 0.04±0.02, 0.06±0.04, and 0.05±0.02 mg/kg As, respectively.

There is considerable variability in As concentrations among individual trees of the same species and within

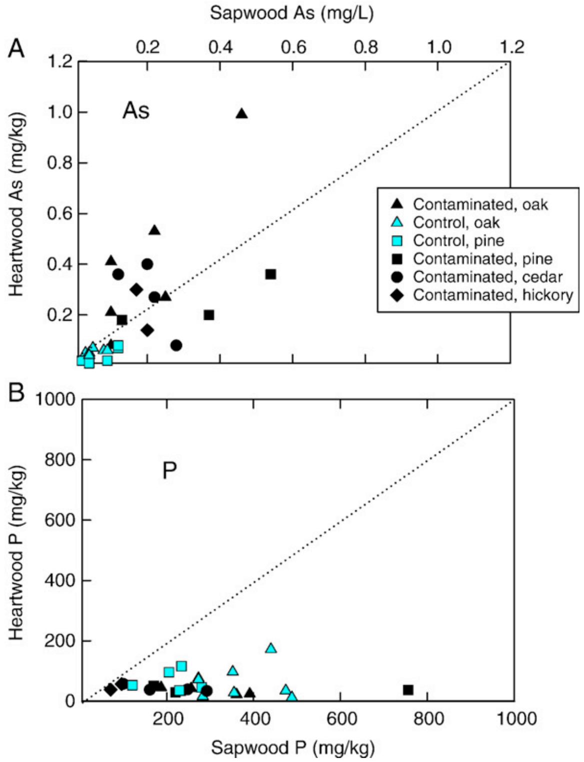

Fig. 2. Comparison of As and P concentrations in sapwood (outer-most rings), and heartwood (inner-most rings).

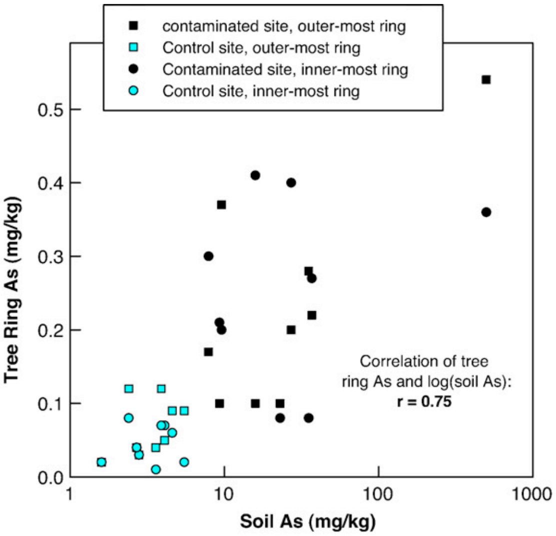

Fig. 3. Soil-tree ring As concentration relationship. Inner-most and outer-most rings represent heartwood and sapwood respectively (see Table 2). Soil As level is the average within 0–30 cm depth. Note the exponential scale for soil As concentration.

different parts of the trees collected from the contaminated zone. These variations obscure any potential systematic difference in As uptake between oak, cedar, hickory, and pine (Table 2). The differences in As concentration within the same tree can be striking. Analyses of sub-sections of the bark from oak tree 14 show a rapid decrease from 2.5 mg/kg at the bark surface to ~0.2 mg/kg in the sub-sample adjacent to the cambium, which is the thin layer between the inner rings of the xylem and phloem of the stem (Fig. 4). This pattern suggests that the generally elevated As levels measured in bark from the contaminated area are limited to the very surface, possibly because of the incorporation of contaminated dust from the area. The range of variations in As concentrations in various tree tissues is narrower at the control sites and there is, again, no detectable difference in As uptake for different species (Table 3).

In contrast to As, P concentrations in tree rings are not significantly different at the contaminated site and the control site (Table 2). There is, however, a systematic difference in the P content of outer and inner rings at both sites: 256±167 mg/kg ($n=15$) and 43±19 mg/kg ($n=15$), respectively at the contaminated site; and 308±109 mg/kg ($n=13$) and 66±46 mg/kg ($n=13$) at the control site. The lower P content of heartwood rings is consistent with nutrient P export from older to younger wood during the conversion of sapwood to heartwood over the life of a tree (Smith and Shortle, 1996).

Concentrations of As in hickory and oak leaves from the contaminated area are comparable to the As content of tree rings (Table 3). The As content of pine and cedar needles, on the other hand, was about an order of magnitude higher. This is consistent with report of As concentrations increasing with the age of successive class needles of pine (Wyttenbach et al., 1996). The higher concentrations of As in the leaves of evergreen trees compared to deciduous trees suggest a continuous supply and accumulation of As over time and retention of evergreen leaves for longer than a single season.

3.3. Radial concentration profiles of As and P

3.3.1. Pine 13

Sapwood in the pine core, empirically differentiated from heartwood by color, contains ~60 annual rings and extends over two-thirds of the stem radius from the pith to the vascular cambium (Fig. 5). The growth pattern of this particular tree is nearly identical to the local pine control chronology derived from five healthy pines in the uncontaminated area (Fig. 1). Concentrations of As in the entire core from pine 13 span a considerable range (0.05–0.75 mg/kg). Within the sapwood, As concentrations are systematically higher in narrow rings produced during low-growth years. When the total As content of each ring is calculated from the concentration and the ring width, it becomes apparent that rings with higher As concentration also contain more As overall (Fig. 5). The radial profile of P shows that the concentration of this nutrient drops dramatically at the independently determined transition from sapwood to heartwood. Within the sapwood section, narrow rings containing elevated As concentrations are generally also higher in P (Fig. 5).

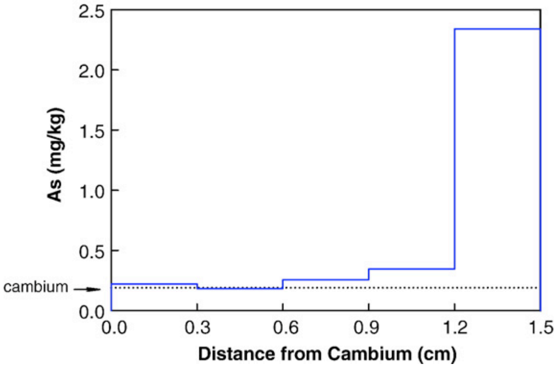

Fig. 4. Arsenic levels in five sub-samples of the bark of Core #14. Note that the As concentration in the inner sub-samples are similar to that in the 2002–2003 rings (i.e., the cambium As level).

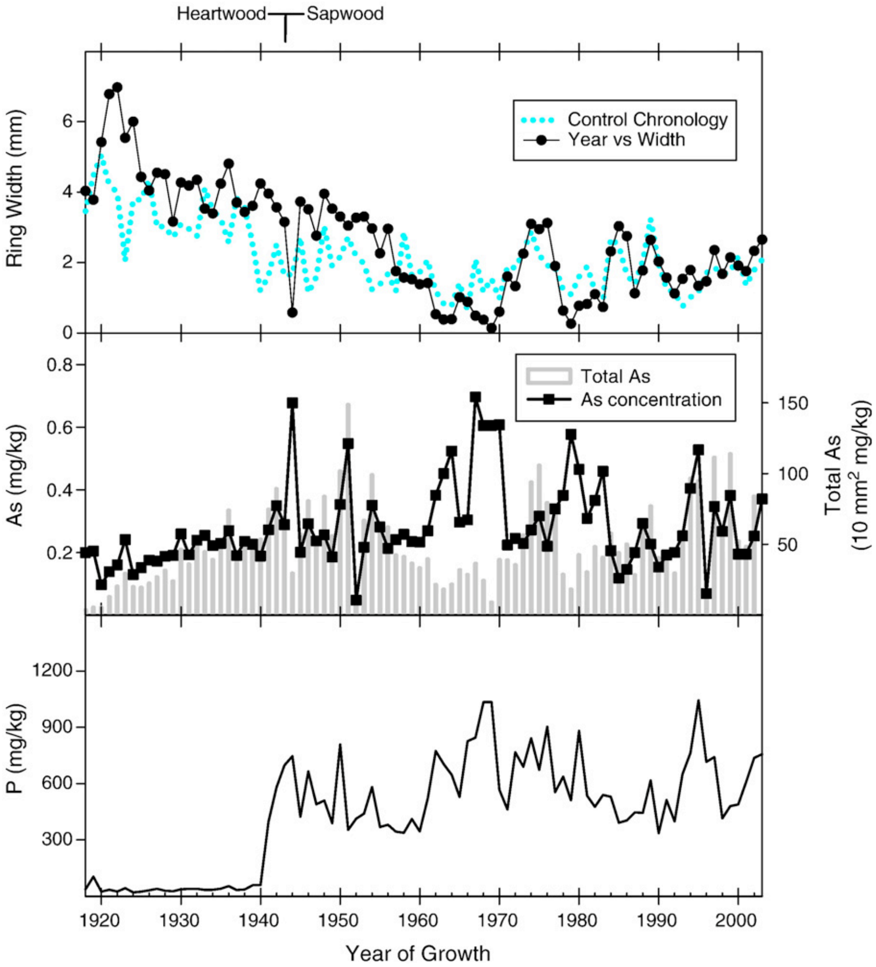

Fig. 5. Tree-ring width and radial profiles of As and P as a function of the chronology for pine 13. Total As is taken as the multiplication of As concentration and the area of annual growth bands.

3.3.2. Oak 14

There are notable differences between the growth pattern of the oak tree analyzed in detail and the control chronology derived from eight oak trees in the Arbor Lake control area (Fig. 6). The growth of the control trees was relatively steady over the past 80 years, whereas oak 14 grew more slowly than the control trees in the 1930s and much faster between 1959 and 1970. Unlike pine tree 13, sapwood in the oak tree core extends to only 10 tree rings. Concentrations of As are relatively low within the larger heartwood section of this core, with the exception of the eight tree rings closest to the heartwood–sapwood transition. The transition is centered on a broad As peak spanning rings formed between 1985 and 1995. The start time of this peak is about 10 years older than the sapwood–heartwood boundary. There is no systematic relation between As concentrations and tree-ring width in this core (Fig. 6). There is also a large increase in P concentrations from the heartwood to the sapwood section in this core.

4. Discussion

4.1. Uptake of P and As from soil

The phosphate content of soils from the contaminated area and the control areas is comparable to P concentrations measured in sapwood. Sapwood:soil enrichment ratios (Smith and Shortle, 2001) for P range from 0.3–7.4. This confirms that the trees are effectively extracting this essential nutrient from the soil through their roots (Bohm et al., 2001). In contrast, As concentrations in sapwood from the contaminated area are 3–4 orders of magnitude lower (0.1–0.5 mg/kg, compared to 106–746 mg/kg for P), even though As

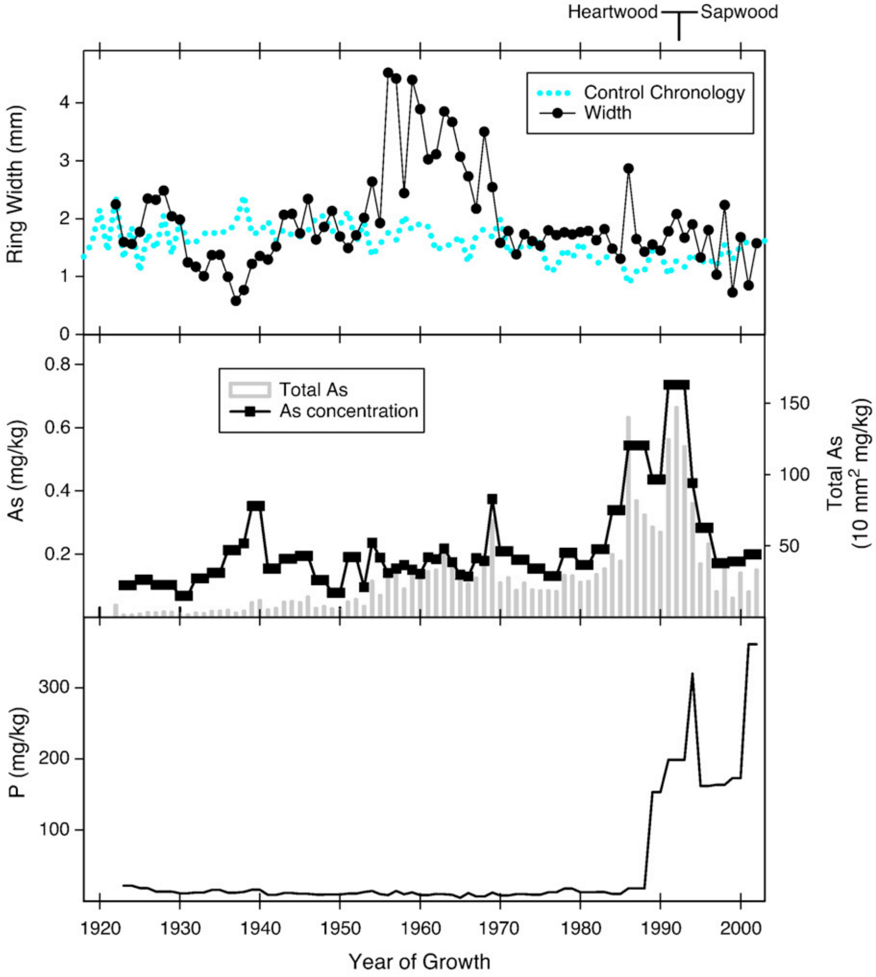

Fig. 6. Tree-ring width and radial profiles of As and P as a function of the chronology of oak 14. Total As is taken as the multiplication of As concentration and the area of annual growth bands.

concentrations in the soil of 8–499 mg/kg are comparable to P levels in the soil.

Although the contrast between P and As uptake by plants has been reported previously, the selective exclusion of As relative to P (with the exception of a few As hyper-accumulating species; e.g. Ma et al., 2001) is striking because As(V) is believed to be the dominant form of As in aerobic soils and a chemical analogue of phosphate P(V). Low As uptake may reflect suppression of the high affinity P(V)/As(V) uptake system at the root-soil interface, which has a higher affinity for P compared to As (Meharg and Macnair, 1992; Meharg et al., 1994). Alternatively, the discrimination against As may reflect reduction of As(V) to As(III) upon entering the tree, which is commonly reported for plants (Mehrag and Whitaker, 2002; Le, 2002), and/or preferential transport in sapwood of P(V) compared to As(III).

The concentration of As in soil and sapwood is roughly proportional in the four tree species that were studied here (Fig. 3). This is consistent with other reported studies on contaminated soils (Baes and McLaughlin, 1984; Jiang and Singh, 1994; Bechtel Jacobs Company LLC, 1998; Martin et al., 2000). Although there is considerable scatter ($R=0.6$), the correlation is encouraging because a response to soil As contamination is a prerequisite for using tree rings as an indicator for historical contamination.

4.2. As contamination and tree growth

The adverse effect of soil contaminated with As on tree growth has been invoked by residents around the Vineland Chemical site as well as remediation personnel to explain the death of many trees at and around the

Vineland Superfund site. In fact during the course of sampling we found many trees with internal decay, though this is not uncommon even under non-contamination conditions. It is known that some plant species that are not resistant to As indeed suffer considerable stress upon exposure, with symptoms ranging from inhibition of root growth to death (Macnair and Cumbes, 1987; Meharg and Macnair, 1991). Bioavailable As concentrations exceeding 5 mg/kg are reported to cause growth defects in plants, while leaf As level of 2.1–8.2 mg/kg are considered toxic for fruit trees (Adriano, 2001). The effect is highly species dependent, however (Macnair and Cumbes, 1987; Meharg and Macnair, 1991).

The trees from the Vineland site don't seem to have been strongly affected by arsenic contamination. Most trees appear to be healthy, although widespread soil contamination started decades ago. The soil As content of most samples are not higher than many agricultural fields or orchards where plants were growing normally (e.g., Martin et al., 2000; Mehrag and Whitaker, 2002). Soil at the site of tree 13 contained ~10 mg/kg As, but this level of contamination evidently did not preclude the pine tree from responding to climatic forcing in the same way as the control trees (Fig. 5). Even the pine that grew in soil containing 500 mg/kg of As doesn't show sign of decay (core #7). The growth pattern of oak tree 14 within the contaminated site did not match that of the controls, but actually exhibited better than average growth between 1950 and 1970. The available observations therefore don't support the notion of an adverse effect of As contamination on tree growth at this site (Fig. 6).

4.3. Implications for historical reconstruction

Monitoring trace metal pollution using tree rings has been controversial for several decades. Although a large number of studies have been conducted, there is still no agreement whether the method yields valid results. It is generally recognized, however, that the incorporation of toxic metals is likely to depend on the tree species as well as the nature of the specific element.

A key issue from the perspective of historical reconstruction is the possibility of contaminant translocation across annual rings *via* rays. Several studies have indeed reported contaminants in rings that had formed many years before contamination (e.g., Lukaszewski et al., 1988; Smith and Shortle, 1996). Radial translocation has been used to interpret concentration profiles of Cd, Zn, Cu and Pb in pine (Symeonides, 1979; Lukaszewski et al., 1988) and oak (Hagemeyer, 1993), which disagreed with known contamination histories. In the case of As, Martin et al. (2000) suggested that there may be active transport of As into the pith and bark based on the much higher As concentration compared to xylem rings. Little is known about As mobility in pine and oak tree stems, however.

Smith and Shortle (1996) argued that some portion of what appears to be "radial translocation" may be due to element transport in all active sapwood rings, rather than in the cambium only. We had hoped the core from pine tree 13 would provide some insights to possible remobilization of As during the flooding period in 1980s. However, the radial As concentration pattern for this core (Fig. 6) suggests that As is probably transported in all sapwood rings. With a particularly wide sapwood section, an exact chronology of soil contamination with As therefore cannot be established through this pine tree-ring profile. This probably also explains why elevated As concentrations in this core pre-date the onset of production of arsenicals in 1950 (Fig. 6). The multiple peaks observed within the sapwood section during low-growth years are probably not an indication of elevated soil As levels at the time, but merely reflect higher sap As concentrations in the rings formed during dry years. It is worth noting that similar correlation of high metal concentrations with narrow rings was also observed for Fe and Ti in *Pinus echinata*, which were remobilized through soil acidification (Baes and McLaughlin, 1984).

In ring porous wood such as oak, however, the transport of minerals should have reached mainly the current decade's rings. Conditions in oak tree 14, with a much narrower sapwood section, should therefore be more favorable for establishing an approximate chronology of As contamination (Hagemeyer, 1993). For reasons that are not clear, the As concentrations in this core rise significantly only after 1980, when the improper storage of arsenicals had stopped and small scale remediation started at the site. We speculate that the pattern may reflect enhanced mobilization of As during initial remediation activities. Alternatively, this may suggest significant lateral translocation of toxic elements in the sapwood and accumulation at the sapwood–heartwood boundary, similar to what has been observed for Cd in oak *Quercus robur* and *Quercus petraea* (Hagemeyer, 1993). The same process may be responsible for radial Pb patterns that couldn't be explained by ambient emission history in a study by Szopa et al. (1973). The movement of toxic substances along the rays during heartwood formation was previously also proposed by Stewart (1966). The coincidence of the As peak in the radial profile with the heartwood–sapwood boundary raises the issue of the suitability of oak for reconstructing the history of arsenic contamination. Further study of the physiological processes governing arsenic uptake, transport and storage is clearly needed.

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